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THE CORROSION OF IRON

BY

J. NEWTON FRIEND, D.Sc., PH.D., F.I.C.

(CARNEGIE GOLD MEDALLIST)

EDITED BY

GEORGE C. LLOYD

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PREFACE

The present volume of *Carnegie Scholarship Memoirs* is devoted wholly to a series of reports by Dr. Friend, dealing with various aspects of the Corrosion of Iron. The various parts were received originally from the author as separate Memoirs, but in view of the fact that they all dealt with the subject of corrosion, it was deemed advisable to regard them as parts of a single work dealing with that subject. The volume should be regarded, therefore, not so much as a text-book on corrosion as a collected series of papers. The Appendix constitutes a preliminary report on the "Relative Corrodibilities of Various Forms of Iron and Steel," an investigation which the author still has in hand, and the detailed results of which will be published later.

G. C. LLOYD.

May, 1922.

CONTENTS

PAGE

THE CORROSION OF IRON. By Dr. J. Newton Friend (Birmingham) 1

Part I. A critical survey of our present knowledge of the corrosion of cast iron 1
What is meant by corrosion 1
The action of acids upon cast iron 8
Action of natural brine and other salts upon cast iron . . . 18
The action of carbon tetrachloride upon cast iron . . . 19
Action of oils upon cast iron 20
The corrosion of cast iron embedded in clay and sand . . . 21
Influence of shape upon the corrosion of cast iron . . . 22
Influence of temperature upon the corrosion of cast iron . . 23
Influence of alloying elements upon the corrodibility of cast iron . 25
Influence of arsenic upon the corrodibility of cast iron . . . 26
Influence of carbon upon the corrodibility of cast iron . . . 27
Influence of cobalt upon the corrodibility of cast iron . . . 29
Influence of manganese upon the corrodibility of cast iron . . 31
Influence of nickel upon the corrodibility of cast iron . . . 33
Influence of phosphorus upon the corrodibility of cast iron . . 34
Influence of manganese and phosphorus upon the corrodibility of cast iron 35
Influence of silicon upon the corrodibility of cast iron . . . 35
Relative corrodibilities of steel, wrought iron, and cast iron . . 37
Gravimetric methods of research 38
Oxygen absorption methods 57
Corrosion and potential difference 70
Results of practical experience of the corrosion of cast iron in service 79

Part II. The protection of iron with paint against subaqueous corrosion 88
Method of experiment 88
The relative proportions of oil and pigment 89
Functions of a pigment 90
The relative values of thin, thick, and multiple coats of paint . 92
Effect of heat treatment of the oil 96
Standard paint 97
The influence of mill scale 98

PAGE

PART III. The influence of strain upon the corrosion of iron . . 103
Material used 106
Densities 107
Solubility in acid 108
Corrosion in neutral solution 110
Influence of carbon 112

PART IV. Influence of temperature upon the rate of corrosion of iron immersed in water 113
Sources of error to be avoided 114
Experimental methods of investigation 118

PART V. The colloidal theory of corrosion 125
Influence of dissolved salts upon corrosion 135
Influence of temperature upon corrosion 140
Action of alcohol 142
Action of poisons 143
Action of radium rays 144
Conclusion 147

APPENDIX. Preliminary report on the relative corrodibilities of various commercial forms of iron and steel 149
White iron rust 150
Scope of the research 151
Results of laboratory tests 152

NAME INDEX 157

SUBJECT INDEX 159

THE CORROSION OF IRON.

PART I.

A CRITICAL SURVEY OF OUR PRESENT KNOWLEDGE OF THE CORROSION OF CAST IRON.

The object of the present memoir is to lay before the reader a concise summary of the various researches that have been carried out from time to time on the corrosion of cast iron. So far as the present writer is aware no such summary has been published within recent years. Owing to the increased use of iron in one form or another, and the proportionate call upon our supplies of coal and iron ore, the problem of the preservation of iron is daily becoming one of greater economic importance.

One of the first essentials to success in solving this intricate problem is a thorough understanding of the causes underlying the corrosion of the metal. It was therefore felt to be desirable to collect together and discuss critically the more important published data on the subject. The difficulty encountered in doing this lies partly in the fact that the information is widely scattered throughout a large number of journals, some of which are obscure and not easy of access. The main difficulty, however, is that much of the work is indexed under other headings which give no indication that corrosion problems have received treatment therein. It is hoped, however, that omissions from this memoir are not serious.

What is Meant by Corrosion.

The destruction of a metal through oxidation or some analogous process is usually termed **corrosion,** and in the case of iron corroding in some neutral medium, the oxidation product is termed **rust.**

The present author distinguishes two types of ferrous corro-

sion, namely, **surrosion** and **erosion.** By surrosion is understood that type of corrosion which results in the production of insoluble oxide or rust, which usually clings to the unattacked metal (French *sur*, on). Erosion, on the other hand, is used to designate such corrosion as that induced by acids, a more or less soluble product resulting, exposing the underlying metal to further attack. In effect, therefore, chemical erosion more closely resembles mechanical erosion than it does surrosion.

When exposed to the combined action of air and water ordinary cast iron readily rusts, becoming coated with a porous friable mass of ferric oxide combined with varying quantities of water. If corrosion has been allowed to proceed for some little time, the underlying layers of rust are usually dark green to black in colour, in consequence of the incomplete oxidation of the metal, namely in the main, to the ferrous condition. Whilst this is a feature of all thick layers of rust surrounding a core of as yet unattacked metal, cast iron, on account of its heterogeneous character and liability to internal galvanic action, is particularly liable to oxidise to ferrous compounds.

As the resulting product is rich in free graphite, and resembles this form of carbon in its colour and softness, the metal is said to have been graphitised.

Graphitisation is less frequently met with in the case of wrought iron or steel, although a few cases have been recorded, and several have come under the notice of the present writer.[1]

For cast iron, however, this has long been a recognised form of corrosion. One of the earliest instances to be recorded is that of some cast-iron cannon-balls raised from a ship which had lain sunk beneath the sea at Karlskrona for some fifty years.[2] The metal had been entirely graphitised and spontaneously heated upon exposure to air for a few minutes.

Both Mallet[3] and Percy[4] quote many interesting cases from various sources, amongst which is the raising in 1740 of cast-iron guns from one of the ships of the Armada, namely, *The Florida*, sunk in 1588 off the coast of Mull. The guns had thus lain in

[1] Probably the earliest recorded is that of a wrought-iron anchor described by Mallet, *British Association Reports*, 1838, p. 259.
[2] Berzelius, *Traité de Chimie*, 1831, vol. iii. p. 274.
[3] Mallet, *British Association Reports*, 1838, p. 260.
[4] Percy, "Metallurgy of Iron and Steel" (Murray, 1864), p. 146.

the sea for 152 years. On scraping away the corroded surface, they became so hot that they could not be touched. Wilkinson[1] states that "the inhabitants of Mull, and all who witnessed the phenomenon, were greatly astonished (as may naturally be supposed); and being themselves unable to solve the mystery, they applied to the surgeon of the ship, as being the most scientific man present; he was, however, as much at a loss to account for such unusual appearances as themselves, but said that although they had been buried in the sea nearly 200 years, yet, as they went down in the heat of action, he supposed they had not had sufficient time to cool."

Wilkinson further gives an account of the raising of guns in 1836 from the *Mary Rose*, an English vessel which sank off Portsmouth in an engagement with the French in 1545. The metal had thus lain exposed to sea-water for nearly 300 years. "The iron guns were of the ancient description, formed of iron bars hooped together with iron rings, and they were all loaded; but the guns being made of wrought or malleable iron, they did not exhibit the same phenomenon as the balls, which were made of cast iron. Those balls, which by their diameter ought to have weighed 30 lbs., were reduced to 19 lbs. 3 ozs. The 8-inch or 70-lb. ones were only 45 lbs., although to external appearance the same as regular shot, until they fell to pieces *red-hot* on exposure to the air."

Mallet mentions that he had in his possession "a piece of similarly changed cast iron from the false keel of the *John Bull*, East Indiaman. In four years this piece of $1\frac{1}{2}$ inch by 4 inches was completely altered through. Its specific gravity is 1·259." He also states that "cannon shots have been found immersed in the sea, near the site of the battle of La Hogue, converted to the depth of an inch into plumbago, or, according to another statement, all through. The battle of La Hogue took place in May 1692; hence these shots have lain in the sea for a period of about 145 years."

Rennie[2] mentions that in 1822 some cast-iron cannon were raised from a pirate vessel which had been sunk off Holyhead

[1] Wilkinson, "On the Extraordinary Effect produced on Cast Iron by the Action of Sea-Water" (London, 1841), pp. 238–239.

[2] Rennie, in discussing Adie's paper, *Minutes of the Proceedings of the Institution of Civil Engineers*, 1845, vol. iv. p. 323.

about one hundred years previously. Although soft when first recovered they hardened upon exposure to air, and when His Majesty King George IV. passed through Holyhead on his way to Ireland a little later, these old guns were used to fire salutes. It is said that they gave louder reports than any other guns!

In 1887 Draper[1] described a case of graphitisation of grey cast iron from a graving slip in the port of Dublin. It had lain at about half tide level for some fifty years, and its upper surface "for a depth of 7 millimetres had been converted into a brown-grey graphitoidal substance, which was without difficulty removed with a knife, leaving the surface of the iron bright and free from any adherent coating. During the operation of removing the easily pulverulent layer, the mass of iron became hot—not hot enough to cause inconvenience in handling, but hot enough to enable it to be very sensibly warm to the touch after the lapse of half an hour." The graphitoidal mass was found to be wholly attracted by a magnet, and readily soluble in dilute hydrochloric acid, evolving some hydrogen and leaving an insoluble residue of graphite.

Amongst the objects dredged up some years ago in the harbour at Brest[2] were some cannon-balls and shells dating from 1652 to 1791, which had therefore been submerged for 100 to 240 years. All were encased in a coat, several inches thick, consisting of sulphides, sand, rust, and calcareous matter, and required a hammer and chisel to break them open. They then fell off like a mould, leaving free the encased objects covered with a viscid black layer, but otherwise little altered in appearance. The iron, however, had been graphitised, could easily be cut with a knife, giving a brilliant black section which rapidly tarnished. It could easily be powdered in a mortar, and its density was only 3·04.

Analysis showed it to consist of:

	Per Cent.
Free iron	36·00
Iron (combined)	12·00
Graphite	13·10
Silicon	2·50
Sulphur	0·325
Chlorine (from the sea)	1·178
Phosphorus	trace
Water, &c.	15·00

[1] Draper, *Chemical News*, 1887, vol. lvi. p. 251.
[2] Lidy, *Engineering News*, 1898, vol. xxxix. p. 85.

A large portion of the iron had clearly been removed, most probably by the solvent action of the sea-water, leaving a mass rich in graphite and ferrous compounds.

Several other similar cases have been described,[1] but the foregoing instances will suffice.

In the majority of cases of natural graphitisation of cast iron, sea-water has constituted the corroding medium, as has already been shown. The oxidation has been slow but prolonged. By employing very dilute acids the process may be greatly accelerated, as was shown by Daniell[2] in 1817. This investigator immersed a cube of grey cast iron in dilute hydrochloric acid; and when the acid was saturated, the cube was taken out and examined. It did not appear to have diminished in volume, and consisted of a soft spongy substance. A specimen of white cast iron, of a radiated fracture, was similarly acted upon, and it required three times as long to saturate the acid as in the case of the grey cast iron. The spongy mass was easily cut with a knife; it was dark grey in colour, somewhat resembling plumbago. "Some of it was put to dry on blotting-paper, and in the course of a minute spontaneously heated and smoked. In one instance, when a considerable quantity had been heaped together, it ignited and scorched the paper. Its properties were not impaired by being left for days and weeks in the solution of iron or in water." Percy[3] mentions that Calvert allowed dilute hydrochloric or acetic acid to act uninterruptedly for two years upon cubes of grey cast iron. The residue rapidly became hot upon exposure to air, presumably owing to oxidation. The following analyses of the cast iron and the residue are given:

	Cast Iron. Per Cent.	Residue. Per Cent.
Iron	93·413	79·960
Carbon	2·900	11·020
Nitrogen	0·790	2·590
Silicon	0·478	6·070
Sulphur	0·179	0·096
Phosphorus	0·132	0·059

Similar effects are obtained with very dilute sulphuric acid.

[1] See Mallet, *loc. cit.*; Le Naour, *Génie*, vol. xxxi. p. 271; Porlier, *Revue de Métallurgie*, vol. xi. p. 793.

[2] Daniell, *Journal of Science and the Arts* (Royal Institution of Great Britain), 1817, vol. ii. pp. 278, 283.

[3] Percy, "Metallurgy of Iron and Steel" (Murray, 1864), p. 146.

If, for example, a rod of cast iron be immersed for some fifty hours in dilute sulphuric acid (one part acid of density 1·19 and three parts water), the outer portion of the metal gradually dissolves, leaving the graphite as a porous, insoluble mass attached to the core of metal. If this layer is dried and scraped off, it rapidly oxidises, rising in temperature to 100° or 120° C. and, in some cases, even to a red heat.[1] Phosphoric acid is stated to produce no such result.[2]

Mallet states that "Mr. Pepys found cast iron similarly changed by the action of pyroligneous acid; and I have myself obtained specimens so produced by this acid in a state of vapour. The same change is produced by the vapour disengaged in the roasting of coffee; and a curious case of similar action of sherry wine on wrought iron and steel is to be found in Thomson's Annals. It is also well known that the cast-iron plates at first used in the interior of Coffey's patent still were rapidly converted into plumbago by the action of the low wines and proof spirits." [3]

Although alternating currents appear to have practically no effect upon the corrosion of cast iron exposed to ordinary tap water,[4] direct currents are known to accelerate the graphitisation of the metal. This was demonstrated by Freund [5] in 1904, who investigated the corrosion of the cast-iron water-mains of Frankfurt am Main and concluded that it was due to the action of stray electric currents. To confirm this he took pieces of the uncorroded metal and made them anodes in dilute solutions of sodium chloride and calcium sulphate, employing platinum as cathodes. A current of 0·1 ampere per square decimetre was passed through the cells, and in one day the iron became coated with a soft, dark green graphitic mass, of density 3·31.

The graphitisation of iron has been made the subject of considerable study by Bauer and Wetzel,[6] who confirm the observa-

[1] Grzeschik, *Chemiker Zeitung*, 1912, vol. xxxvi. p. 505.
[2] Kohn, "Iron Manufacture," p. 65. Quoted by Turner, "The Metallurgy of Iron" (Griffin, 1908), p. 426.
[3] Mallet, *British Association Reports*, 1838, p. 260.
[4] Bergius and Krassa, *Zeitschrift für Elektrochemie*, 1909, vol. xv. p. 712.
[5] Freund, *Zeitschrift für angewandte Chemie*, 1904, vol. xvii. p. 45.
[6] Bauer and Wetzel, *Mitteilungen Königlichen Materialprüfungsamt*, Berlin, 1916, vol. xxxiv. p. 11.

tion that it is not confined to grey cast iron, but that white and mottled varieties likewise exhibit this form of corrosion under suitable conditions. Experiments are described which have been carried out with various forms of cast iron treated electrically under different conditions. In one series the metals were suspended in cylindrical glass vessels of the dimensions shown in Fig. 1 and connected with the terminals of a 2·2 volt accumu-

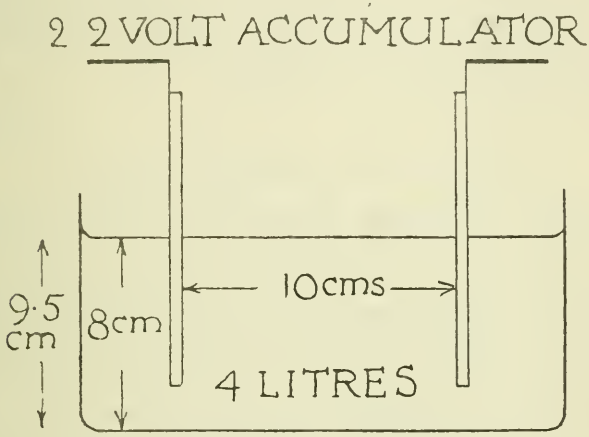


Fig. 1.—Bauer and Wetzel's Apparatus (1916).

lator. The cast iron measured $10 \times 2 \times 1$ cubic centimetres and possessed the composition given on p. 23. The duration of the experiments was eight days, and the following solutions were employed :

1. Distilled water.
2. Tap water.
3. Artificial sea-water.
4. 10 per cent. magnesium chloride solution.[1]
5. 10 per cent. magnesium sulphate solution.[2]

The cast-iron cathodes were not attacked, neither did the anodic cast iron in distilled water show any signs of graphitisation. In the tap water the anode showed traces of attack. The action was strongly marked in the magnesium sulphate solution,

[1] Namely, 106·7 grammes $MgCl_2.6H_2O$ per litre.
[2] Namely, 102·3 grammes $MgSO_4.7H_2O$ per litre.

whilst in the chloride solutions (Nos. 3 and 4) it reached a maximum, penetrating almost half way to the centre of the metal.[1]

Graphitisation is facilitated also by galvanic action caused by contact with a less corrodible metal (see p. 78). Mallet[2] quotes a case from Thomson's Annals of 1825 "in which bars of cast iron of 3 inches broad by 1 inch thick, which formed protectors to the copper of a vessel, to the amount of about $\frac{1}{100}$ of its surface, were, in a voyage of not quite five months, to Jamaica and back, converted into plumbago to the depth of half an inch; it heated on being scraped and exposed to the air when the ship first went into dock."

The Action of Acids upon Cast Iron.

It has been abundantly demonstrated during the last decade that the behaviour of various forms of iron towards neutral corroding media is usually no indication whatever of the resistance those metals will offer towards acid attack, and *vice versa*. Thus a high nickel steel is very resistant to ordinary corrosion and to the action of sulphuric acid as well. A 12 to 13 per cent. chromium steel is even more resistant to neutral corrosion, and is appropriately termed "stainless." On the other hand, sulphuric acid dissolves it with ease.

It is of importance to inquire, therefore, what kind of resistance cast iron is capable of offering to acid attack, and whether or not one form of cast iron is superior to another in this respect. Mention has already been made of the fact that very dilute acids tend to cause the graphitisation of cast iron (see p. 5)—a fact first demonstrated by Daniell in 1817. With somewhat more concentrated solutions the iron dissolves, evolving hydrogen and hydrocarbons, leaving an insoluble residue consisting mainly of graphite in the case of grey cast iron. Crystallised silicon may also be present in the residue.[3]

Percy[4] mentions that T. H. Henry had likewise found "crystallised silicon amongst the graphitic scales in the residue

[1] Judging by the photographs in the original paper. Numerical data are not given.

[2] Mallet, *British Association Reports*, 1838, p. 261.

[3] Richter, *Berg- und Hütten-männisches Jahrbuch*, 1862, vol. xi. p. 288.

[4] Percy, "Metallurgy of Iron and Steel" (Murray, 1864), p. 145.

obtained by the action of hydrochloric acid on pig iron." Tilden [1] has found iron silicide in this way. When, on the other hand, white iron is subjected to acid attack, hydrogen and hydrocarbons are evolved, and " a light, insoluble residue, which is dark brown while moist and light brown when dry, is obtained."

It may be taken as a general rule [2] that cast irons containing large flakes of graphite are more susceptible to acid attack, whilst close-grained white iron is less so. For this reason white cast iron is employed for acid-resisting plant. Turner finds that as the metal becomes closer in the grain and lower in phosphorus, the effect of acids is less marked. With a close-grained iron corresponding very nearly to the old Staffordshire pig a metal is obtained which will withstand acids remarkably well.

The explanation appears to be [3] that ferrite is more readily attacked by acids than the carbide, so that white cast iron which is rich in carbide is more resistant. Grey cast iron, on the other hand, is more porous, and upon immersion in acid the ferrite is dissolved out from the pearlite, leaving the graphite, cementite, and phosphide more or less *in situ*, so that the outward shape of the mass remains substantially the same. This is particularly interesting in view of the fact that alkalies, on the other hand, appear to attack the carbide, leaving ferrite undissolved, as mentioned on p. 14.

Owing to its brittleness, white cast iron cannot always be employed for acid-resisting plant, and vessels are therefore made consisting of grey cast-iron shells with a *chilled* white inner surface. The product thus possesses the toughness of the grey iron coupled with the resistance of the white.[4]

Mallet [5] was aware that cast iron rich in silicon is highly resistant to hydrochloric acid, and this is confirmed by Turner,[6] who states that " when iron contains 10 per cent. of silicon and upwards, it resists the action of acids so well that it has been

[1] Tilden, *Proceedings of the Birmingham Philosophical Society*, 1882, vol. iii. p. 203.

[2] Turner, *Journal of the Iron and Steel Institute*, 1915, No. I. p. 364 ; 1908, No. I. p. 76.

[3] Turner, " The Metallurgy of Iron " (Griffin, 1915), p. 455. Kröhnke, *Metallurgie*, 1910, vol. vii. p. 674.

[4] Lunge, *Journal of the Iron and Steel Institute*, 1908, No. I. p. 83.

[5] Mallet, *British Association Reports*, 1838, p. 277.

[6] Turner, " The Metallurgy of Iron " (Griffin, 1915), p. 426

proposed to employ this kind of metal for the production of pipes, taps, and other articles in chemical works." Turner also passes on to say that "when cast iron containing much phosphorus is dissolved in acids, the residue generally contains phosphorus in combination with iron in some form in which it is not attacked by ordinary solvents."

It is noteworthy that whilst diluted sulphuric acid vigorously attacks cast iron, concentrated acid does not attack it, until the SO_3 concentration exceeds that required for the formula H_2SO_4. In this latter concentration the metal tends to disintegrate (see p. 13). Thus, for example, acid of concentration corresponding to 90° Twaddell is very corrosive towards cast iron; at 98° Twaddell the metal is but little attacked, whilst at 100° to 110° Twaddell practically no action takes place.[1] With wrought iron, on the other hand, all concentrations of acid are active until the SO_3 content exceeds that required for the formula H_2SO_4 by some 27 per cent.[2] The fuming acid thus produced has little or no action on the metal.

This is a very striking illustration of the fact, to which reference is made in the sequel, that no one form of iron can be considered as offering the maximum resistance to all types of corrosion (see p. 37).

According to Stead,[3] the reason why concentrated sulphuric acid does not continuously act upon iron is due to the fact that the acid produces a protective layer of sulphate, insoluble in the concentrated acid, so that the underlying metal is preserved from further attack. This is in harmony with the experimental results of Larsson[4] on the influence of concentrated sulphuric acid on iron, but, as indicated below, cannot be the whole explanation.

The following results, obtained by Messrs. H. W. Catch and L. B. Hargest, working under the direction of Dr. F. Johnson and the author in the laboratories of the Birmingham Municipal Technical School, are of interest as showing the effect of progressively varying concentrations of sulphuric acid upon mild steel and grey cast iron of two grades under strictly comparable

[1] Davis, *Journal of the Iron and Steel Institute*, 1908, No. I. p. 80.
[2] Knietsch, *Berichte*, 1901, vol. xxxiv. p. 4090.
[3] Stead, *Journal of the Iron and Steel Institute*, 1908, No. I. p. 77.
[4] Larsson, *Teknisk Tidskrift*, 1893, p. 32.

conditions. The specimens measured $4 \cdot 5 \times 0 \cdot 8 \times 0 \cdot 65$ centimetres and weighed approximately 22 grammes. They were each immersed in beakers containing 500 cubic centimetres of acid for eight hours at 15° C., after which they were carefully scraped, dried, and weighed, the loss in weight being taken as a measure of the acid attack.

Analyses of Cast Irons and Steel.

	No. 2.	No. 7.	Mild Steel.
Graphite	2·75	2·75	...
Combined carbon . . .	0·55	0·61	0·21
Silicon	2·28	1·72	0·034
Manganese	0·69	0·75	0·80
Sulphur	0·076	0·085	0·061
Phosphorus	1·04	1·06	0·041

The results were as follow :

Concentration [1] of H_2SO_4 . .	O	N/2	N	2N	3N	4N	5N
Mean Loss [2] of cast irons—							
No. 2 . . .	0·0245	7·597	9·463	**10·77**	10·47	9·90	9·08
No. 7 . . .	0·0125	4·588	6·826	7·886	8·34	**8·94**	8·65
Mild steel . . .	0·0083	0·334	0·524	0·765	0·994	1·241	1·466

It will be observed that in both cases the rate of solution of cast iron rises to a maximum and then falls, although the concentration of acid producing the maximum effect is not the same, but apparently varies with the composition of the metal. On the other hand, the rate of solution of the steel steadily rises with the acid concentration, and in no concentration does it approach the high values found for the cast iron. If Stead's explanation of the fall in solution velocity of cast iron in high acid concentration is correct, there is no apparent reason why the same phenomenon should not occur with steel. The phenomenon is probably more complex than would appear at first sight.

Hydrochloric acid is particularly active in attacking cast iron. Carulla [3] mentions a case, which came under his own observation, in which " the plug of a cast-iron cock, used to keep back ferrous liquor containing a very small percentage of free hydrochloric acid, was acted upon to the depth of one-eighth of an inch in a

[1] N = normal, *i.e.* 49 grammes per litre.

[2] Mean of two specimens each, expressed as grammes per square decimetre of exposed surface.

[3] Carulla, *Journal of the Iron and Steel Institute*, 1908, No. I. p. 71.

few months." In practice, generally, hydrochloric acid is found to have an exceedingly corrosive action on iron.[1]

The effect of progressive variation in the concentration of hydrochloric acid upon the rate of solution of cast iron and mild steel is shown by the following results obtained by Catch and Hargest in precisely similar experiments to those already detailed with sulphuric acid. Samples from the same bars of cast iron were treated for eight hours at 17° C. with the following effects:

Concentration [2] of HCl	O	N	2N	4N	6N	7N	8N	9N	10N
Mean Loss [3] of cast irons—									
No. 2 .	0·009	14·47	17·69	**20·77**	18·26	18·08	18·85	18·39	11·54
No. 7 .	0·009	10·67	14·61	**19·45**	19·36	17·22	15·78	14·29	9·03
Mild steel	0·0053	0·612	0·786	0·968	1·957	3·31	5·38	9·94	13·27

As with sulphuric acid the rate of solution at first rises with the concentration in the case of the two cast irons. A maximum effect is reached with the 4N solution in both cases, after which further concentration of acid reduces the rate of solution. The steel, on the other hand, shows progressively increased solution velocity.

According to Wood,[4] tannic acid attacks cast iron readily, and Messrs. Turner Bros. cover with gun-metal or brass all ironwork, such as shafts, &c., which are likely to come into contact with tannin.

It has long been known that both wrought iron and steel frequently become brittle after exposure for a short time to acid attack. The phenomenon was first studied by W. H. Johnson,[5] who directed the attention of the Manchester Literary and Philosophical Society to it during the Session 1873 to 1874. In the latter year Osborne Reynolds further investigated the problem and showed that the induced brittleness is due to occluded hydrogen. A similar effect is produced by exposing iron to the action of concentrated caustic soda solution at 100° C.

[1] Prost (*Revue Universelle des Mines*, vol. xi. p. 308. Abstracted in the *Journal of the Iron and Steel Institute*, 1891, No. I. p. 428) gives analyses of the residues obtained when white pig iron is attacked by various concentrations of hydrochloric acid.

[2] N = normal, *i.e.* 36·5 grammes of HCl per litre.

[3] Mean of two specimens each, expressed as grammes per square decimetre of exposed surface.

[4] Wood, *Journal of the Iron and Steel Institute*, 1908, No. I. p. 84.

[5] Johnson, *Proceedings of the Royal Society*, 1875, vol. xxiii. p. 168. Brittleness had previously been observed by Daniell, in 1817, in tempered steel after acid attack.

It has been suggested that the brittleness is due to the more rapid absorption of hydrogen by the intercrystalline cement, whereby a certain amount of expansion occurs, forcing the crystals apart and reducing their cohesion.[1] Cast iron is not so sensitive as the purer forms of the metal, possibly on account of the altered solubility of hydrogen in iron containing alloyed silicon.[2] Thus, for example, a few hours' exposure to very dilute sulphuric acid will render wrought-iron plates very brittle, whilst to obtain the same effect with cast iron an exposure for nine days in a more concentrated acid is necessary. In every case the brittleness is lost on annealing or on allowing the metal to stand in the dry for some time.

It is interesting in this connection to recall the warning issued by Knietsch,[3] that whilst cast-iron vessels are suitable for the preparation of hydrated sulphuric acid, it is dangerous to employ them for the fuming acid, as the metal is liable to suddenly burst or disintegrate, often with a loud noise. This is attributed by Knietsch to the penetration of the acid into the pores of the metal, and the liberation of sulphur dioxide, hydrogen sulphide, and eventually of carbon dioxide, which remains in the cast iron under high pressure, ultimately leading to its disruption. This would appear to be supported by the fact that upon fracture of the metal the two first-named gases are readily detectable by their odour.

A similar disruption of cast-iron vessels has been reported by Cumming [4] as taking place in contact with acid consisting approximately of

	Per Cent.
Nitric acid	50
Sulphuric acid	45
Water	5

The cast-iron vessels which burst had a wall thickness of from 1 to 1½ inches and a capacity of 55 and more cubic feet. They were used under a working air pressure of not more than 60 lbs. per square inch, and when the vessels disrupted they appeared to disintegrate into fragments rather than to be blown out. There

[1] Andrew, *Transactions of the Faraday Society*, 1919, vol. xiv. p. 232; 1914, vol. ix. p. 316.

[2] Ledebur, *Stahl und Eisen*, 1887, vol. vii. p. 681.

[3] Knietsch, *Berichte*, 1901, vol. xxxiv. p. 4090.

[4] Cumming, *Journal of the Society of Chemical Industry*, 1919, vol. xxxviii. p. 31-T.

appeared to be no appreciable corrosion, but on breaking a washed piece of the iron the odour of acid was very obvious. Micrographic examination by Desch showed that the acid had penetrated to a depth of about one-third of the thickness, and small clusters of crystalline salts could be seen in different places in the interior. It is therefore concluded by Cumming that "the expansive force of these crystals, growing in the interior of the iron, was doubtless responsible for the disruption of the iron, even though the actual corrosion of the metal was comparatively negligible."

Dilute solutions of chromic acid appear to have no action upon cast iron. Sealed tubes containing the above have been kept by the present author for fourteen years, and the cast iron still appears bright and untarnished.

The Action of Alkaline Solutions upon Cast Iron.

Whilst dilute solutions of alkali hydroxides, for example, $\frac{1}{50}$-normal sodium hydroxide, or $\frac{1}{30}$-normal ammonium hydroxide, entirely inhibit the corrosion of wrought iron or steel immersed in them, cast iron becomes coated with a thin, bronze-coloured oxide.[1]

Mention has already been made of the fact that acids, when attacking grey cast iron, preferentially dissolve the ferrite, leaving graphite, cementite, and phosphide as a residue (see p. 9). Alkalies, on the other hand, attack the cementite. Turner[2] mentions that in the case of cast-iron pans under his observation which had failed while in use for evaporating alkali, the ferrite was left whilst the carbide from the pearlite had been preferentially attacked.

When made the anode in a solution of caustic soda or potash cast iron is, of all the common varieties of iron, the most easily attacked,[3] passing into solution as sodium (or potassium) ferrate, Na_2FeO_4 (or K_2FeO_4).

In 1886 Venator[4] gave the results of several valuable series

[1] Friend, *Journal of the Iron and Steel Institute*, 1908, No. II. p. 8.

[2] Turner, "The Metallurgy of Iron" (Griffin, 1915), p. 455.

[3] Poggendorf, *Pogg. Annalen*, 1841, vol. liv. p. 161; Haber, *Zeitschrift für Elektrochemie*, 1900, vol. vii. pp. 215, 724; Pick, *ibid.*, p. 713.

[4] Venator, *Chemiker Zeitung*, 1886, vol. x. pp. 319, 389.

of experiments on the influence of caustic soda upon various forms of iron. A commercial form of soda was employed, being contained in a silver vessel of approximately $1\frac{1}{2}$ litres capacity. The pieces of metal weighed about 50 grammes and measured $6 \times 2 \times 0{\cdot}5$ centimetres, having a superficial area of 32 square centimetres. They were completely submerged in the soda whether the latter was fused or in solution, and it was found that no electrolytic action took place between the metals and the silver. The analyses of the specimens employed and the results obtained are given in Tables I. and II.

TABLE I.—*Analyses of Metals used by Venator* (1886).

	Cast Iron.	Wrought Iron.	Steel.
Carbon	3·15	0·040	0·365
Silicon	1·98	0·026	0·182
Phosphorus	0·724	0·102	0·007
Sulphur	0·049	0·132	0·007
Manganese	0·540	trace	not given

The caustic soda used was an ordinary commercial variety possessing the following composition:

	Per Cent.
NaOH	94·36
Na_2CO_3	1·85
NaCl	3·05
Na_2SO_4	0·63
Fe_2O_3 and Al_2O_3	0·11

TABLE II.—*Action of Commercial Caustic Soda upon Iron and Steel.* (*Venator*, 1886.)

Series.	Metal.	Caustic Soda.	Temperature. Degrees C.	Loss in Weight. Grammes.	Mean Loss.	Relative Loss.
A	Cast iron	Fused, anhydrous	400	0·1980 0·2290 0·1636	0·1969	100
	Wrought iron	,,	,,	0·1700 0·1585 0·1695	0·1660	84
	Steel	,,	,,	0·2120 0·1765 0·2330	0·2072	105

TABLE II.—(*continued*).

Series.	Metal.	Caustic Soda.	Temperature. Degrees. C.	Loss in Weight. Grammes.	Mean Loss.	Relative Loss.
B	Cast iron	Fused, anhydrous	350	0·1215 0·1615 0·1875	0·1568	80
	Wrought iron	,,	,,	0·0445 0·0250	0·0348	18
	Steel	,,	,,	0·0175 0·0250 0·0155	0·0193	10
C	Cast iron	80 per cent. solution	200	0·7792 0·2602 0·1645	0·3680	187
	Steel	,,	,,	0·1305 0·1370 0·1590	0·1422	72
D	Cast iron	46 per cent. solution	150	0·0180 0·0510	0·0345	18
	Wrought iron	,,	,,	0·3190 0·0705 0·1890	0·1928	98
	Steel	,,	,,	0·1350 0·1370 0·1245	0·1322	67
E	Cast iron	20 per cent. solution	150	nil	0·0000	0
	Wrought iron	,,	,,	0·0660 0·0815 0·0695	0·0723	37
	Steel	,,	,,	0·0155 0·0125 0·0120	0·0133	7

Consideration of the foregoing results shows that whilst in several cases different specimens of the same type of iron under similar conditions offer very different resistances towards corrosion, in the main the following generalisations may be regarded as correct:

1. Comparing series A and B it is evident that the action of fused caustic soda is rapidly intensified as the temperature rises above 350° C. in the case of wrought iron and steel. The effect is in the same direction with cast iron, but is not so marked. At 350° C. the order of attack is cast iron, wrought iron, steel;

but at 400° C. there is little to choose between the steel and cast iron, and the wrought iron is not greatly superior to either.

2. With increasing dilution of the caustic soda with water, the effect upon the cast iron is markedly reduced, becoming nil with a 10 per cent. solution at 150° C. The other forms of iron are also less readily attacked, the steel proving the more resistant of the two.

Owing to a serious accident at Thann, where a cast-iron vessel gave way under the influence of fused caustic soda under pressure, whereby an attendant was almost fatally injured, Scheurer-Kestner [1] was led to investigate the reaction. Pieces of wrought iron and cast iron were subjected to the action of pure, fused caustic soda for five hours with the following results:

TABLE III.—*Action of Fused Caustic Soda upon Iron.* (*Scheurer-Kestner*, 1896.)

Temperature. Degrees C.	Pressure (Atmospheres).	Percentage Losses in Weight.	
		Wrought Iron.	Cast Iron.
210	1	0·27	0·15
250	1	0·743	0·347
250	under autoclave pressure	0·936	0·424

Unfortunately no analyses of the metals are given, so that it is impossible to draw detailed conclusions. It would appear that pressure stimulates the corrosive action of the fused alkali, and that cast iron resists the action more successfully than wrought iron.

THE ACTION OF HYDROGEN PEROXIDE ON CAST IRON.

Pure iron catalytically decomposes dilute solutions of pure hydrogen peroxide, without itself undergoing corrosion.[2] Cast

[1] Scheurer-Kestner, *Bull. Soc. Chim.*, 1896, (3), vol. xv. p. 1250.

[2] Moody, *Transactions of the Chemical Society*, 1906, vol. lxxxix. p. 729. The fact that solutions of pure hydrogen peroxide do not corrode pure forms of iron was known to Thénard in 1830 (Thénard, *Traité de Chimie*, Brussels, 8th edition, 1830, vol. i. p. 212), but the fact appears to have been lost sight of until Moody redirected attention to it.

iron, on the other hand, whilst it decomposes hydrogen peroxide, is itself rapidly attacked. Since it contains appreciable quantities of sulphur, phosphorus, &c., it is easy to see that these elements would, under the influence of a powerful oxidiser, give rise to acids and thus accelerate the corrosion of the metal.[1]

In solutions of hydrogen peroxide in $\frac{1}{50}$-normal sodium hydroxide or $\frac{1}{30}$-normal ammonium hydroxide solutions the purer forms of iron remain unattacked, although they effect the liberation of oxygen from the peroxide. Cast iron in these circumstances becomes coated with a thin layer of bronze-coloured oxide.[2]

Action of Natural Brine and Other Salts upon Cast Iron.

The attention of engineers is directed by Menzel [3] to the action of certain natural brines upon the cast-iron portions of pumps. In one case investigated by him the cast iron was severely attacked within two years, and this was traced to the presence of carbon dioxide and hydrogen sulphide in solution. Analysis showed that one litre of the fresh liquid taken from the centre of the shaft contained 6·57 cubic centimetres of free CO_2 and 2·62 cubic centimetres of free H_2S. After passage through the pump and pipes, however, the brine was entirely free from these gases. Examination of the cast iron showed the presence of rust and iron sulphide, together with a little basic iron sulphate. On thoroughly aerating the brine prior to passage through the pump, namely by allowing it to flow over series of cascades, these corrosive gases were removed, after which the brine ceased to have any serious action upon the metal.

Kempson states that his firm have found "no appreciable corrosion of cast iron in the sections of the sulphate of ammonia still (Coffey's principle). The sections are exposed to the action of layers of boiling alkaline liquid, and above of steam, ammonia, sulphuretted hydrogen, and various other gases. No difference is perceptible between the action of the hot gases and liquor." Corrosion has been observed in the cast-iron pipes between the

[1] Friend, *Journal of the Iron and Steel Institute*, 1908, No. II. p. 25; *Nature*, 1906, vol. lxxiv. p. 540; Moody, *ibid.*, p. 564.

[2] Friend, *loc. cit.*

[3] Menzel, *Zeitschrift für das Berg-, Hütten-, und Salinen-wesen*, 1907, vol. lv. p. 447.

tar still and water level in the condensers, and this is probably due to the presence of ammonium chloride, which readily dissociates, yielding free hydrochloric acid.[1]

For ammonia stills, cast iron seems everlasting.[2] Carulla instances a plant that had been in use for eighteen years without sign of wear in any of the numerous cylinders. Fryer[3] states that he had used a cast-iron pot for the concentration of a solution of calcium chloride at about 340° F., but found that "the only visible effect was to clean and brighten the inside of the pot, without forming any peroxide; and the chloride, when poured out and left to solidify, was as white as when put in."

The Action of Carbon Tetrachloride upon Cast Iron.

This is a problem of considerable interest and importance to those who employ cast-iron extractors in the removal of fat from bones, using carbon tetrachloride as solvent. Bolis[4] has shown that when cast iron is kept in contact with dry boiling carbon tetrachloride for ten hours, the loss in weight of the metal is inappreciable. The surface becomes coated with a dark layer which apparently preserves the underlying metal from attack. If, however, the carbon tetrachloride is saturated with moisture, the metal is appreciably attacked at the boiling temperature, whilst a mixture of carbon tetrachloride with one-third of its volume of water caused cast iron to lose some 5 per cent. in weight in the course of ten hours at the boiling point. Since bones may contain very varying quantities of water it is interesting to inquire what effect this may have upon the corrosion of the extractor. To determine this, Bolis heated together carbon tetrachloride and various kinds of bone mixtures in vessels containing pieces of cast iron and obtained the following results;

	Loss in Weight of Cast Iron. Per Cent.
1. Good quality, dry bones	0·15 to 0·30
2. Good quality, wet bones	0·275 „ 0·40
3. Poor quality, wet bones	0·49 „ 0·825
4. Poor quality, very wet bones	1·05 „ 1·25

Evidently, therefore, unless dry materials can be used, cast iron is very liable to be destroyed under these conditions.

[1] Kempson, *Journal of the Iron and Steel Institute*, 1908, No. I. p. 83.
[2] Carulla, *ibid.*, p. 71; Jackson, *ibid.*, p. 82.
[3] Fryer, *ibid.*, p. 81.
[4] Bolis, *Chemiker Zeitung*, 1906, vol. xxx. p. 1117.

Action of Oils upon Cast Iron.

Holde[1] gives the results of an investigation into the action of various lubricating oils upon cast iron under a steam pressure of 10 atmospheres. The method of experiment consisted in putting 20 to 30 grammes of the oil in an agate dish, placed within an autoclave. A cast-iron plate measuring 3 × 0·4 centimetres in area was immersed in the oil, and the whole heated until the pressure rose to 10 atmospheres. After two, four, and six hours respectively the plate was removed, rubbed with filter paper and washed with ether, and finally weighed. The acidity of the oil after six hours' treatment in this way was determined whenever possible—the darkening of the oil by decomposition sometimes rendered this impossible.

The results obtained are given in the following table:

Table IV.—*Action of various Lubricating Oils upon Cast Iron under the Influence of Superheated Steam at a Pressure of* 10 *Atmospheres.* (*Holde*, 1895.)

Oil.	Loss in Weight (in Mgs.) of Cast Iron after			Percentage Acidity (calculated as Oleic Acid).	
	Two Hours.	Four Hours.	Six Hours.	Original Oil.	After Six Hours.
Scotch thin mineral oil	3	3	4	0·05	0·06
Thick, dark mineral oil	4	4	4	1·42	1·42
Crude rape oil . .	0[2]	5[2]	41[2]	0·85	37
Refined rape oil, I. .	15	66	205	1·34	..
Refined rape oil, II. .	4·5[2]	49	118	0·35	..
Tallow . . .	0·5[2]	20·5[2]	168	1·57	71
Mixture of two parts dark mineral and one part refined rape oils	2·4[3]	8[3]	14[3]	1·44	11·8

These results are of considerable importance to engineers. It will be observed that whilst the mineral oils have but a small action upon the metal, the fatty lubricants, rape oil and tallow, exert a very appreciable corrosive influence. This, of course, is precisely what one might expect in view of the fact that mineral

[1] Holde, *Mitteilungen aus den Königlichen technischen Versuchsanstalten*, Berlin, 1895, Supplement I.

[2] Mean of two tests. [3] Mean of three tests.

oils are essentially hydrocarbons and hence incapable of saponification under the experimental conditions to fatty acids. The fatty lubricants, however, undergo saponification, and the increase in their acidity, as given in the final column of Table IV., is very pronounced.

The Corrosion of Cast Iron Embedded in Clay and Sand.

Of considerable interest are the data supplied by Bauer and Wetzel,[1] who exposed for a period of fifteen months bars of cast iron to various corroding media, contained in large, glass cylindrical jars, 18 centimetres in diameter and 18 centimetres in height.

The dimensions and analysis of the metal are given below, and the results of the corrosion tests in Table V.

Cast Iron used by Bauer and Wetzel (1916).

Dimensions of plates, 10 × 2·5 × 2 c.c.

Analysis.

	Per Cent.
Combined carbon	1·40
Graphite	2·30
Silicon	1·68
Manganese	1·69
Sulphur	0·054
Phosphorus	0·083
Copper	0·04

Table V.—*Corrosion of Cast Iron Bars under different Conditions.* (*Bauer and Wetzel*, 1916.)

Vessel No.	Condition of Experiment.	Loss in Weight in 15 Months. Grammes.	Relative Corrosion.
1	Distilled water	6·23	100
2	Tap water enriched with $CaSO_4$	7·61	122
3	Clay saturated with distilled water	10·38	167
4	Clay saturated with tap water enriched with calcium sulphate	10·20	164
5	Sand saturated with distilled water	5·62	90
6	Sand saturated with tap water enriched with calcium sulphate	6·36	102

[1] Bauer and Wetzel, *Mitteilungen Königlichen Materialprüfungsamt*, Berlin, 1916, vol. xxxiv. p. 37.

The foregoing conditions may be considered as analogous to such as obtain in many water-logged soils, and it is interesting to note the very appreciable effect of the clay. Ordinarily, of course, clay in a stiff condition is regarded as affording high protection for the metal it encases, whilst sand, on account of its porosity, offers little or none.

Influence of Shape upon the Corrosion of Cast Iron.

Mallet,[1] in 1840, drew attention to the interesting fact that in several series of experiments in which plates of cast iron were immersed in clear sea-water for 387 days, the thicker plates measuring $5 \times 5 \times 1$ cubic inches corroded much less rapidly than thinner plates, measuring $5 \times 5 \times 0{\cdot}25$ cubic inches, but precisely similar in chemical composition. This difference was most marked in the graphitic or grey cast irons, and least in the white varieties.

The following table indicates the type of result obtained:

Table VI.—*Influence of Thickness upon Corrosion.* (*Mallet*, 1840.)

Specimen No.	Character of Cast Iron.	Corrosion Factors of Plates measuring	
		5 × 5 × 1 Cubic Inches.	5 × 5 × 0·25 Cubic Inches.
1, 2	Dark grey	39·2	83·4
12, 13	Bright grey	19·8	100·9
18, 19	Mottled	45·6	69·8
26, 27	Mottled	46·9	63·6
30, 31	White	58·5	63·6

Mallet explains this on the ground that the thinner castings had cooled more rapidly and more irregularly than the thicker, so that they were less homogeneous. Consequently on immersion in sea-water the number of voltaic couples set up was proportionately increased, and corrosion proceeded apace.

[1] Mallet, *British Association Reports*, 1840, p. 235.

Influence of Temperature upon the Corrosion of Cast Iron.

This is a subject that has been very much neglected. In 1915 a few data were published by Bauer and Wetzel,[1] who determined the relative corrodibilities of samples of cast iron and steel in tap water, as supplied to their laboratories, and in the same water after it had been softened by the permutit process. The experiments were carried out by suspending plates of the metals in glass vessels for twenty-five days. Each vessel contained some 350 cubic centimetres of water and one metallic plate. In the experiments at 50° and 80° C. the vessels were fitted with reflux condensers, to prevent loss by evaporation, and maintained at the desired temperature in a glycerine bath which was heated up each morning and cooled each evening. In Series A the water was renewed every day, and in Series B the same water was used throughout.

The dimensions and analyses of the plates are given in Table VII. The analyses of the tap water and softened water are given in Table VIII., whilst Table IX. gives the results obtained, expressed as the mean losses in weight (grammes) of four separate plates each.

Table VII.—*Plates used by Bauer and Wetzel*, 1915.

Dimensions.

Cast iron	4·5 × 3·0 × 0·2 c.c.
Steel	4·5 × 3·0 × 0·075 c.c.

Analyses.

	Cast Iron.	Steel
Combined carbon	0·62	0·04
Graphite	3·08	...
Silicon	2·40	0·01
Manganese	0·89	0·59
Phosphorus	0·663	0·034
Sulphur	0·09	0·025
Copper	0·074	0·162

[1] Bauer and Wetzel, *Mitteilungen Königlichen Materialprüfungsamt*, Berlin, 1915, vol. xxxiii. p. 1.

TABLE VIII.—*Analyses of the Water used by Bauer and Wetzel* (1915), *expressed as Milligrammes per Litre.*

	Before Softening.	After Softening.
Silica	15	11
Iron oxide and alumina	trace	trace
Lime	98	nil
Magnesia	10	4
Carbon dioxide	192	199
SO_3	28	28
Chlorine	34	36
Potash and soda	58	234

Total hardness [1]—before softening . . . 11·2
after softening . . . 0·6

TABLE IX.—*Losses in Weight of Cast Iron and Steel at Various Temperatures.* (*Bauer and Wetzel*, 1915.)

(All weighings are expressed in grammes.)

Water.	Temperature. Degrees C.	Series A.		Series B.	
		Cast Iron.	Steel.	Cast Iron.	Steel.
Tap	16	0·650	0·0632	0·0280	0·0423
Softened	16	0·570	0·0660	0·0370	0·0525
Tap	50	0·1858	0·1665	0·1436	0·1185
Softened	50	0·2075	0·2018	0·1664	0·1441
Tap	80	0·1708	0·1769	0·1976	0·1794
Softened	80	0·2215	0·2560	0·1757	0·2119

These results are interesting for several reasons. They illustrate the enormously increased corrosive action of water as the temperature is raised. The actual increase per degree cannot of course be calculated, because the effect was intermittent, the vessels being allowed to cool over night.

It will be observed, too, that in most of the cases the softened water is more corrosive than the untreated water. This is not to be wondered at, since alkali salts have taken the place of calcium and magnesium salts during the softening process, as is

[1] Expressed as 1 part $CaCO_3$ per 100,000 parts of water.

evident from the data in Table VIII. This, of course, is the whole basis of the softening process, and the present writer can, from the results of his own experiments, substantiate the greater corrosiveness of certain softened waters. Finally, it will be noted that the cast iron is sometimes superior to the steel and sometimes inferior, in its resistance to corrosion.

Influence of Alloying Elements upon the Corrodibility of Cast Iron.

Owing to the complex nature of cast iron, the introduction of alloying elements may affect the corrodibility of the metal in one or both of two ways.

1. **Indirect Action.** Many elements tend to influence the condition of the carbon in cast iron. Thus, for example, silicon endeavours to throw it out as graphite, thereby rendering the metal more porous and susceptible to internal galvanic activity, and hence to certain corrosive influences, such, for example, as acid attack. Such an effect is indirect and quite independent of any influence exerted *per se* upon the corrodibility of the alloy.

2. **Direct Action** is beautifully illustrated by sulphur. This is always a dangerous element to have in cast iron, existing as it does almost exclusively as sulphides which are readily oxidisable, yielding sulphureous compounds which markedly accelerate corrosion, quite apart from any indirect action due to the tendency of sulphur to cause the carbon to appear as graphite.

Although during the last few years a considerable amount of work has been done on the influence of alloyed elements on steel, the problem of cast iron has not received the attention it deserves. In the following sections are briefly summarised all the researches bearing on this point which have come under the author's notice. It will be observed that such small changes in chemical composition as normally occur in cast irons, apart from those connected with the condition of the carbon, have but a small effect upon the corrodibility of the metal. For example, a variation of the silicon content from 1·2 to 2 per cent. has no appreciable effect provided the amounts of graphite and combined carbon remain constant. Any variation in the graphite, however, causes a marked alteration in corrodibility.

This is a point of great importance from an economic point of view, and one to which Mallet carefully directed attention in 1843.

It is thus apparent that in the majority of cases the influence of alloyed elements in such small amounts as occur in ordinary cast irons is of an *indirect* rather than a *direct* character in so far as corrodibility is concerned. If, of course, several per cent. of certain alloying elements are present, a very marked effect may be exerted upon the corrodibility. Thus high silicon contents of the order of 10 per cent. render the metal very resistant. But such alloys are not cast irons in the ordinary acceptation of the term and do not therefore call for discussion in these pages.

Influence of Arsenic upon the Corrodibility of Cast Iron.

Very few data are extant as to the influence of alloyed arsenic upon the corrodibility of cast iron. Such information as we do possess points to the fact that arsenic is not a desirable constituent.

Mallet[1] in 1840 mentions that "soon after Algiers was taken by the French, some ancient shot and shells were sent to France to be recast, which had been discovered in the arsenal. They were found, however, unfit for service; the metal of which they were composed was full of minute cavities, so brittle as to be easily pulverised, white and lamellar. Analyses of the shot and shells gave the following results in 1000 parts:

	Shot.	Shells.
Carbon	0·010	0·015
Arsenic	0·270	0·098

"They contained neither sulphur, manganese, calcium, nor silicon. Specific gravity of shot = 7·650, of shells = 7·585. The cast-iron alloy of which they were formed was found by Berthier[2] to oxidate, when exposed to air and water, with unusual rapidity; he supposes these projectiles to have been cast in Spain, of iron made from mispikel or arseniuret of iron."

Whilst it is clear from the analyses given above that the metal

[1] Mallet, *British Association Reports*, 1840, p. 269.
[2] Berthier, *Annales des Mines*, vol. xi. p. 512.

termed by Mallet *cast* iron was not really such in the ordinary acceptation of the term, the observation is of interest as constituting probably the first authentic record of the enhanced corrodibility of iron caused by the presence of arsenic. In this connection it is perhaps desirable to mention that Heyn and Bauer [1] obtained a somewhat analogous result with pieces of steel superficially alloyed with arsenic by heating in a current of hydrogen arsenide for $1\frac{1}{2}$ hours at 900° C. The metal was then exposed to the action of 1 per cent. sulphuric acid, and was found to be attacked considerably more vigorously than the untreated specimens. The authors very rightly point out, however, that superficial impregnation with arsenic as in the above process does not necessarily yield a product similar in its power of resisting corrosion to that obtained by standard methods of preparing homogeneous alloys. This observation is all the more important in view of the fact that, some three years later, Burgess and Aston [2] found that alloyed arsenic, in quantities ranging from 0·29 to 4·14 per cent., tends to retard the corrosion of electrolytic iron both in acid solution and when exposed to neutral corrosion.

It must be admitted, therefore, that the whole subject is obscure and deserving of further attention.

Influence of Carbon upon the Corrodibility of Cast Iron.

Carbon is usually present in cast iron in two main forms, namely, as *combined* carbon, or as free carbon in the form of *graphite*. In the former case the carbon is chemically combined with the iron, or perhaps in part with some other element alloyed with it, and cannot be distinguished by the unaided eye from the other constituents. The fracture thus appears homogeneous and white, whilst the metal itself is hard and dense. In grey cast iron, on the other hand, the carbon is present in the chemically free or uncombined graphitic form, and imparts to the metal its characteristic, grey appearance, and, when powdered, its unctuous feel. It renders the compact metal porous and soft,

[1] Heyn and Bauer, *Journal of the Iron and Steel Institute*, 1909, No. I. p. 109.
[2] Burgess and Aston, *Eighth International Congress of Applied Chemistry*, 1912 (New York).

thereby enhancing its liability to corrode. When immersed in dilute acid or in saline solutions, the graphite flakes act cathodically towards the adjacent particles of metal which, being more readily oxidised, pass rapidly into solution or undergo oxidation to rust, according to circumstances.

In 1840 Mallet [1] not only showed by quantitative experiment that grey cast iron is more corrodible than white when immersed in sea-water, but also directed attention to the fact that if specimens of the white metal are placed in metallic contact with the grey in sea-water, the loss of the former by corrosion is greatly reduced, whilst that of the latter is increased.

His results were as follow : [2]

White cast iron, alone	100
Grey cast iron, alone	143

In his monumental researches, published in 1843, Mallet [3] has shown that in general grey cast iron is more corrodible than the chilled metal when exposed to ordinary atmospheric influences, although the exact opposite was found in clear river water. As regards acid attack it may be taken as a general rule [4] that the least resistant cast irons are those containing large flakes of graphite, whilst close-grained white iron is most resistant. As early as 1817 Daniell [5] pointed out that in his experiments white cast iron dissolved much more slowly than the grey in diluted acids. For this reason white or chilled cast iron is recommended for the construction of acid-resisting plant [6] (see p. 85). Harbord states that in those industries where boiling sulphuric acid has to be used, as, for example, gold refining, white iron pans give very much better results than grey ; indeed the white iron is the only type that can be used.

Very little systematic quantitative work has been carried out on this important problem, and the following results obtained by Catch and Hargest are therefore of special interest and value.

[1] Mallet, *British Association Reports*, 1840, p. 266.

[2] Expressed relatively to the white cast iron. Mallet gives his results as fractions of an inch of surface removed by corrosion.

[3] Mallet, *loc. cit.*, 1843, p. 1. See this Memoir, p. 43.

[4] See Turner, *Journal of the Iron and Steel Institute*, 1915, No. I. p. 364 ; 1908, No. I. p. 76.

[5] Daniell, *Journal of Science and the Arts*, 1817, vol. ii. p. 278.

[6] Turner, *loc. cit.* ; Harbord, *Journal of the Iron and Steel Institute*, 1908, No. I. p. 77 ; Stead, *ibid.*, p. 78.

Specimens of sand-cast and chilled cast iron measuring $4 \cdot 5 \times 1 \times 1$ centimetres were exposed to various corroding media, their losses in weight being determined in the usual manner.

The analyses of the metals were as follow :

	Sand-cast.	Chilled.
Graphite.	2·65	0·78
Combined carbon	0·48	2·32
Silicon	1·71	1·59
Manganese	0·48	0·48
Sulphur	0·094	0·089
Phosphorus	1·28	1·26

Metal.	Corroding Medium.	Duration of Test.	Mean Loss in Weight.[1]	Relative Corrosion.
Sand cast .	Alternate wet and dry	3 months	2·769	100
Chilled .		,,	2·665	96
Sand cast .	3 per cent. sodium chloride	3 months	1·138	100
Chilled .		,,	1·166	103
Sand cast .	0·1 per cent. H_2SO_4	8 hours[1] at 15 ° C.	1·183	100
Chilled .			0·250	21
Sand cast .	0·5 per cent. H_2SO_4	8 hours[1] at 15 ° C.	3·314	100
Chilled .			0·506	15

These results are in full agreement with those recorded above as obtained by early investigators.

Influence of Cobalt upon the Corrodibility of Cast Iron.

A study of the influence of cobalt upon the corrosion of iron is one of considerable interest from both commercial and scientific points of view. Increased attention is being paid to the industrial production of cobalt, and the close similarity in chemical and physical properties between this metal and nickel naturally stimulates inquiry into the relative merits and demerits of the two. Nickel is known to reduce the tendency of steel to corrode both in acid and in neutral corroding media. In the case of cast iron, addition of 1 per cent. of nickel reduces

[1] Mean of two specimens each, expressed as grammes per square decimetre of area exposed.

the solubility of the alloy in dilute sulphuric acid (see p. 33), but further addition of the metal yields a more corrodible alloy, on account of the simultaneous increase in graphitic carbon.

No research appears to have been carried out with a view to determining the effect of added cobalt on the resistance of cast iron towards neutral corroding media, although the results of a few experiments in 1 per cent. sulphuric acid are detailed by Bauer and Piwowarsky.[1] The alloys were prepared by the addition of metallic cobalt—prepared by reduction of the oxide with charcoal—to molten pig iron of Swedish origin and possessing the following composition :

	Per Cent.
Combined carbon . . .	1·10
Graphite	2·80
Silicon	0·69
Manganese	0·18
Phosphorus	0·048

The alloys were cast into bars, and small specimens measuring $1 \times 1 \times 1{\cdot}5$ cubic centimetres were immersed in 1 per cent. sulphuric acid for twenty-four hours at room temperature, and the losses in weight determined. A portion of the remelted pig iron was similarly cast into bars without addition of cobalt and was used as standard. The results obtained were as follow :

TABLE X.—*Influence of Cobalt upon the Solubility of Cast Iron in 1 per Cent. Sulphuric Acid.* (*Bauer and Piwowarski*, 1920.)

Composition of Metal.			Percentage Loss in Weight.	Relative Corrosion.
Combined Carbon.	Graphite.	Cobalt.		
1·11	2·80	0·0	18·7	100
1·03	2·86	0·0	17·9	
1·06	2·85	0·92	16·2	88
0·95	2·92	0·90	15·8	
1·28	2·54	1·88	13·8	76
1·30	2·58	1·92	14·0	

It is interesting to note that, in contradistinction to nickel, cobalt tends to increase the carbide formation and hence to reduce

[1] Bauer and Piwowarsky, *Stahl und Eisen*, 1920, vol. xl. p. 1300.

the graphite. The total effect is thus to enhance the resistance of the metal towards acid attack. The effect of the cobalt, *per se*, upon the corrosion is less than that of nickel, 1 per cent. of which was found, in a series of precisely similar tests (see p. 33), to reduce the corrosion of cast iron from 100 to 80.

This, however, is precisely what one might expect in view of relatively weaker influence exerted by cobalt in steels.

These results are in accord with those obtained by Burgess and Aston [1] on the influence of alloyed cobalt on electrolytic iron both in acid solution and in neutral corrosion.

Influence of Manganese upon the Corrodibility of Cast Iron.

Heyn and Bauer [2] carried out two series of experiments with cast irons of manganese content ranging from 0·46 to 3·08 per

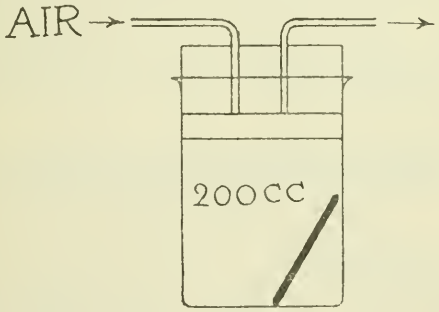


Fig. 2.—Heyn and Bauer's Arrangement for Series I. (1908).

cent. The metal was cast into plates measuring 3·85 × 4·75 centimetres in area and 0·45 centimetre in thickness. In the first series of experiments the plates stood at the bottom of a gas jar containing 200 cubic centimetres of tap water, and a constant stream of air was passed through the vessel, as shown in Fig. 2.

In the second series of experiments the plates were suspended from glass rods in a 5-litre enamelled cast iron tank (Fig. 3),

[1] Burgess and Aston, *Eighth International Congress of Applied Chemistry*, 1912 (New York).

[2] Heyn and Bauer, *Mitteilungen Königlichen Materialprüfungsamt*, Berlin, 1908, vol. xxvi. p. 31.

30 × 16 centimetres in area, the top of the plates lying 2·4 centimetres below water-level, and exposed to still tap water the surface of which had free access to the air. All the experi-

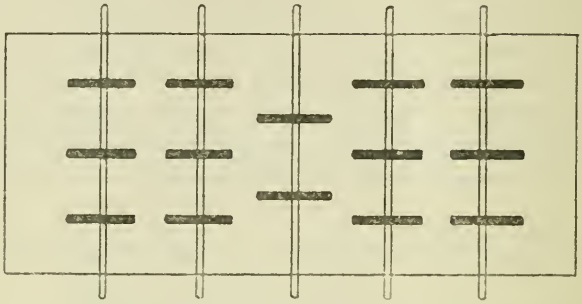


Fig. 3.—Heyn and Bauer's Arrangement for Series II. (1908).

ments lasted twenty-two days and were conducted at room temperature.

The losses in weight were taken as a measure of corrosion, which was as follows :

Table XI.—*Influence of Manganese upon the Corrosion of Cast Iron in Water.* (*Heyn and Bauer,* 1908.)

Composition of Metal.						Relative Corrosion. Series I.	Relative Corrosion. Series II.	Mean.
Combined Carbon.	Graphite.	Si.	S.	P.	Mn.			
0·48	2·97	3·06	0·059	0·072	*0·46*	100	100	*100*
0·59	2·97	2·43	0·077	0·071	*0·70*	92	92	*92*
0·49	3·17	2·56	0·076	0·072	*0·99*	100	91	*96*
0·48	3·02	2·48	0·065	0·082	*1·90*	94	94	*94*
0·60	3·10	2·61	0·052	0·082	*2·83*	96	89	*93*
0·70	2·79	2·46	0·071	0·053	*3·08*	89	96	*93*

A consideration of the above table shows that, as the elements other than manganese are present in fairly constant amount, any influence upon the corrodibility exerted by the increased amount of manganese should be readily detectable.

It is evident that the manganese tends very slightly to reduce the corrodibility of the metal.

Influence of Nickel upon the Corrodibility of Cast Iron.

It has long been known that the addition of nickel to iron and steel renders the product less liable to corrosion whether in neutral or in acid-corroding media. It is interesting to inquire therefore as to the effect of nickel upon the corrodibility of cast iron.

Data on this important point are remarkably scanty. The only reliable work appears to be that of Bauer and Piwowarsky,[1] who, however, confined their studies to the action of 1 per cent. sulphuric acid solution, and did not attempt any water, wet and dry, or sea-water tests.

The specimens were prepared by adding electrolytic nickel to molten pig iron of Swedish origin, and possessing the composition given on p. 30. Although the temperature was only some 50° C. above the melting point of the pig iron, the nickel readily alloyed. The mixture was cast into bars, and small specimens measuring $1 \times 1 \times 1{\cdot}5$ cubic centimetres were cut and exposed for twenty-four hours to the action of a 1 per cent. solution of sulphuric acid at room temperature. The remainder of the metal was used for analysis, hardness and numerous other physical tests. A portion of the remelted pig iron was similarly cast into bars but without addition of nickel, and was used as standard. The results obtained were as follow:

Table XII.—*Influence of Nickel upon Solubility of Cast Iron in 1 per Cent. Sulphuric Acid.* (*Bauer and Piwowarsky*, 1920.)

Composition of Metal.			Percentage Loss in Weight.	Relative Corrosion.
Combined Carbon.	Graphite.	Nickel.		
1·11	2·80	0·0	18·7	100
1·03	2·86	0·0	17·9	
1·01	2·87	0·85	14·3	80
1·07	2·83	0·89	14·9	
0·86	2·93	1·24	14·7	81
0·84	2·89	1·26	14·9	
0·57	3·14	1·92	15·1	85
0·59	3·10	1·98	15·9	

[1] Bauer and Piwowarsky, *Stahl und Eisen*, 1920, vol. xl. p. 1300.

It is interesting to note that the addition of about 1 per cent. of nickel effects an appreciable reduction in the corrodibility of the metal. With 2 per cent. of nickel the corrodibility begins to increase again, probably on account of the higher proportion of graphite, the counter effect of which more than neutralises the increased resistance of the added nickel.

Influence of Phosphorus upon the Corrodibility of Cast Iron.

Heyn and Bauer [1] carried out two series of experiments with cast irons of phosphorus content ranging from 0·071 to 3·38 per cent. in a precisely similar manner to their manganese tests, detailed on p. 31. The experiments lasted twenty-two days and were conducted at room temperature. The results were as follow:

Table XIII.—*Influence of Phosphorus upon the Corrosion of Cast Iron in Tap Water.* (*Heyn and Bauer*, 1908.)

Composition of Metal.						Relative Corrosion. Series I.	Relative Corrosion. Series II.	Mean.
Combined Carbon.	Graphite.	Si.	S.	Mn.	P.			
0·59	2·97	2·43	0·077	0·70	*0·071*	100	100	*100*
0·63	2·74	2·50	0·122	0·73	*0·59*	100	102	*101*
0·80	2·60	2·56	0·168	0·56	*0·71*	111	101	*106*
0·79	2·55	2·33	0·161	0·61	*1·23*	102	103	*103*
0·29	2·71	2·38	0·166	0·48	*2·11*	114	99	*107*
0·34	2·20	2·37	0·152	0·55	*3·38*	105	99	*103*

The phosphorus apparently makes but little difference. This is surprising in view of the pronounced retardation of corrosion found by Diegel [2] in the case of steel plates exposed to sea-water in Kiel harbour. By increasing the phosphorus content from 0·062 to 1·08 per cent. the corrosion fell from 100 to 81.

[1] Heyn and Bauer, *loc. cit.*, 1908, vol. xxvi. p. 31.

[2] Diegel, *Verhandlungen des Vereins zur Beförderung des Gewerbfleisses*, 1903, vol. v. p. 157.

Influence of Manganese and Phosphorus upon the Corrodibility of Cast Iron.

Heyn and Bauer [1] carried out a few experiments with plates of cast iron containing varying quantities of manganese and phosphorus. The plates were exposed to tap water for twenty-two days at room temperature under conditions precisely similar to those already detailed under manganese (p. 31, see Figs. 2 and 3).

Table XIV.—*Influence of Manganese and Phosphorus upon the Corrosion of Cast Iron in Water.* (*Heyn and Bauer*, 1908.)

Composition of Metal.						Relative Corrosion. Series I.	Relative Corrosion. Series II.	Mean.
Combined Carbon.	Graphite.	Si.	S.	Mn.	P.			
0·63	2·74	2·50	0·122	*0·73*	*0·59*	100	100	*100*
0·81	2·59	2·56	0·134	*1·39*	*1·17*	98	103	*101*
0·77	2·41	2·39	0·127	*2·25*	*2·30*	89	106	*98*
0·94	2·00	2·38	0·077	*4·57*	*3·45*	124	112	*118*

The only metal exhibiting a pronounced variation in corrosion is the last one.

Influence of Silicon upon the Corrodibility of Cast Iron.

For many years chemists have recognised that the presence of alloyed silicon tends to retard the corrosion of iron. Thus Mallet [2] in 1838 directed attention to the fact that cast iron, rich in silicon, is less readily attacked by acids. In 1908 Jouve [3] showed that alloys of iron and silicon, containing some 20 per cent. of the latter element, are remarkably resistant to acid attack. Turner [4] mentions that pig iron, containing 18 per cent. of silicon, has been exposed to the fumes of the laboratory at Birmingham University for many years without showing any appreciable

[1] Heyn and Bauer, *loc. cit.*, 1908, vol. xxvi. p. 31.
[2] Mallet, *British Association Reports*, 1838, p. 277.
[3] Jouve, *Journal of the Iron and Steel Institute*, 1908, No. III. p. 310.
[4] Turner, "Metallurgy of Iron" (Griffin, 1908), p. 421.

corrosion. From 16 to 20 per cent. of silicon appears to be the optimum concentration for yielding corrosion-resisting alloys.[1] But alloys such as these are not cast iron in the ordinary acceptation of the term.

Friend and Marshall [2] have studied the influence of varying the silicon content of cast iron from 1·24 to 2·28 per cent. upon the corrodibility of the metal. This range is interesting for two reasons:

1. It covers many of the various silicon contents usually met with in commercial cast irons, so that the results are not purely of academic importance.

2. The silicon is never so great as to interfere with the nature of the carbon content.

This latter is an important point. As is well known, the presence of silicon tends to throw out the carbon as graphite; consequently, unless particular care is taken to keep the carbon in the same chemical and physical condition, the influence of the silicon *per se* upon the corrodibility of the metal must be affected by the proportion of graphitic carbon, and the results rendered misleading.

From the analyses given in Table XV., it is evident that the elements other than silicon were present in the cast irons in very uniform proportions.

TABLE XV.—*Analyses of Cast Irons used by Friend and Marshall* (1913).

Cast Iron No.	Combined Carbon.	Graphite.	Si.	S.	Mn.	P.
1	0·65	2·70	*1·24*	0·096	0·63	0·99
2	0·68	2·65	*1·29*	0·093	0·75	1·05
3	0·65	2·55	*1·45*	0·082	0·89	1·04
4	0·67	2·70	*1·55*	0·079	0·86	1·02
5	0·61	2·75	*1·72*	0·085	0·75	1·06
6	0·51	2·60	*2·04*	0·115	0·86	1·09
7	0·55	2·75	*2·28*	0·076	0·69	1·04

[1] See Kowalke, *Proceedings of the American Electrochemical Society*, 1917; also Turner, *Journal of the Iron and Steel Institute*, 1908, No. I. p. 76; Stead, *ibid.*, p. 78.

[2] Friend and Marshall, *Journal of the Iron and Steel Institute*, 1913, No. I. p. 381.

The irons were sawn into rectangular blocks measuring $4{\cdot}8 \times 1{\cdot}1 \times 1{\cdot}5$ cubic centimetres and weighed about 60 grammes. They were polished with emery paper, and exposed to various corroding agencies, in a precisely similar manner to those already mentioned on p. 11. The results were as follow :

TABLE XVI.—*Influence of Silicon upon the Corrosion of Cast Iron.* (*Friend and Marshall,* 1913.)

Cast Iron No.	Silicon per Cent.	Relative Corrosion in				
		Tap Water. 17 Weeks.	Wet and Dry. 15 Weeks.	3 per Cent. NaCl. 13 Weeks.	0·05 per Cent. H_2SO_4. 13 Weeks.	0·5 per Cent. H_2SO_4. 13 Weeks.
1	1·24	100	100	100	100	100
2	1·29	81	116	92	105	100
3	1·45	101	103	95	100	99
4	1·55	100	100	99	98	99
5	1·72	99	99	101	104	102
6	2·04	95	103	101	104	106
7	2·28	88	105	88	101	106

The result is somewhat surprising in showing that the variation in silicon *per se* exerts no appreciable influence upon the corrodibility of the metal either in neutral or in acid media *within the limits experimented upon.*

RELATIVE CORRODIBILITIES OF STEEL, WROUGHT IRON, AND CAST IRON.

Which of the various commercial forms of iron or steel is the least liable to corrode? This is a question of perennial interest and importance, and one which each generation may have to determine for themselves. Every modification or improvement in the methods of manufacture of the metals is liable to influence either favourably or adversely their power of resisting corrosion. A careful perusal of the following pages will probably serve to convince the reader that no simple answer can be given to this question. For some purposes cast iron is the most resistant metal to employ ; for others, wrought iron ; and for yet others, steel. A very striking illustration of this is given on p. 10. In

the following paragraphs an attempt is made to group together for purposes of comparison the results obtained by different investigators upon exposing various forms of iron to attack under the following conditions :

1. Neutral corroding media at rest.
2. Neutral corroding media in motion.
3. Acid corroding media.

1. *Relative Corrodibilities of Steel, Wrought Iron, and Cast Iron in Neutral Corroding Media at Rest.*

a. Gravimetric Methods.

One of the most magnificent researches carried out last century on the relative corrodibilities of wrought iron and various forms of cast iron was that undertaken by Mallet under the auspices of the British Association. The results are given in a detailed report published in 1840,[1] but which, possibly on account of its bulk, has not received the consideration from metallurgists that it so thoroughly deserves.

A plate of wrought iron, measuring 5×5 square inches in area and 0·875 inch in thickness was taken as the standard, and its loss in weight after immersion in sea-water for 387 days at a temperature ranging from 46° to 58° F. (8° to 14·5° C.) was taken as unity, all other losses in weight being expressed relatively thereto, and termed the *index of corrosion*. If this index is multiplied by 100, as in the accompanying tables, it is converted into what the present author[2] many years ago termed the *Corrosion Factor*, and which is now in common use in expressing the relative corrodibilities of two or more metals. The following corroding media were used :

Series I.—The metals were immersed in clear sea-water in Kingstown Harbour for 387 days—from August 3, 1838, to August 26, 1839. Temperature range, 8° to 14·5° C. Mean density of the water, 1·02780 at 15·4° C. One specimen of wrought iron, seventy-five specimens of cast iron.

Series II.—The specimens were immersed in foul sea-water

[1] Mallet, *British Association Reports*, 1840, pp. 221–308.
[2] Friend, "The Corrosion of Iron and Steel" (Longmans, 1911), p. 276.

close to the mouth of the great Kingstown main sewer. The bottom consisted of putrid mud. Exposure dated from August 3, 1838, to August 26, 1839, that is, 387 days. Temperature range 8° to 145° C. One specimen of wrought iron, twelve specimens of cast.

Series III.—The specimens were immersed in warm sea-water in a tank heated by circulation of water from a boiler. Temperature, 115° F. (48° C.). Exposure dated from August 6, 1838, to December 1, 1838, that is, 117 days. One specimen of wrought iron, twelve specimens of cast.

Series IV.—The specimens were immersed in foul river-water, namely in mid-stream of the river Liffey at Dublin. Exposure dated from August 6, 1838, to January 13, 1840 ; that is, 383 days. Temperature range, 36° to 61° F. (3° to 16° C.). One specimen of wrought iron, twelve specimens of cast.

Series V.—The specimens were sunk in clear, fresh water of the river Liffey, above the tidal limits. Bottom consisted of fine granite sand. Temperature range, 32° to 68° F. (0° to 20° C.). Exposure dated from August 4, 1838, to August 20, 1839 ; that is, 381 days. One specimen of wrought iron, twelve specimens of cast.

In the following table[1] is given a summary of the results obtained for all such cast-iron plates as measured $5 \times 5 \times 1$ cubic inches, reduced to a common period of immersion of 387 days,[2] and expressed relatively to the wrought-iron plate immersed in sea-water, but measuring $5 \times 5 \times 0{\cdot}875$ cubic inches.[3] Analyses of the metals are not given by Mallet, which is distinctly unfortunate.

Consideration of Table XVII. reveals several highly interesting features.

1. Despite the wide variations in the different types of cast iron experimented upon, the relative rates of corrosion of comparable specimens in any one of the vertical columns bear a close similarity to one another. Thus, for example, the corrosion

[1] Adapted from that given by Mallet, *loc. cit.*, p. 298.

[2] Calculated on the assumption that corrosion is directly proportional to the duration of exposure.

[3] All the wrought-iron plates were rather less than 1 inch in thickness, but the error thereby introduced is probably inappreciable.

factors of the first four cast irons in sea-water lie between 57·6 and 66·6, whilst those of the five chilled specimens lie between

TABLE XVII.—*Summary of Results obtained by Mallet* (1840).

Metal.	Corrosion Factors.				
	Series I. Sea-water.	Series II. Foul Sea-water,	Series III. Warm Sea-water.	Series IV. Foul River-water.	Series V. Clear River-water.
Wrought iron (standard) .	100·0	118·6	134·7	68·8	12·3
Calder hot-blast cast iron .	57·6	29·7	7·7	41·3	7·4
do. chilled . .	72·2	79·4	76·0	55·6	11·7
Pentwyn hot-blast cast iron .	60·8	20·1	38·0	38·2	11·6
do. chilled . .	78·0	88·5	55·1	58·5	13·8
Apedale hot-blast cast iron .	64·0	7·3	31·1	16·1	10·6
do. chilled . .	56·9	20·7	65·4	38·4	10·8
Arigna cold-blast cast iron .	66·6	16·4	26·5	59·3	10·3
do. chilled . .	63·2	107·5	82·6	59·1	17·4
Hardest cast iron procurable, chilled	51·7	19·2	5·0	44·2	10·8
Mixed Calder and Pentwyn .	73·4	24·3	42·7	41·7	7·7
Mixed Arigna and Pentwyn .	60·5	25·0	40·8	45·7	11·5
Cast iron, skin removed .	77·6	127·8	131·3	64·4	23·5

51·7 and 78·0. A few striking exceptions occur, as is usually the case in work of this kind, and may perhaps be due to some irregularity in the metal or some local peculiarity in the conditions of corrosion. Thus the Calder hot-blast iron and the hardest chilled cast iron appear remarkably resistant in Series III., whilst the chilled Arigna cold-blast metal proved highly corrodible in foul sea-water. Apart from these, however, the above generalisations appear fairly correct.

2. The chilled metals are generally more susceptible to corrosion than the unchilled. This is rather unexpected, but Mallet[1] explains it on the ground that the exterior of chilled castings is not homogeneous. Hence "the voltaic action produced at the surface of chilled cast iron, by its want of homogeneity, increases the corrosion of the metal by menstrua, to a greater extent than its great density and hardness, and small amount of uncombined carbon, are capable of retarding its corrosion, in comparison with other sorts of cast iron."

[1] Mallet, *loc. cit.*, p. 235.

3. The wrought iron corrodes very much more seriously in all the waters, other than clear river-water, than do the cast irons. The superiority of the latter for drainage purposes would thus appear to be established, and this is in harmony with the results of modern practice (see p. 83).

4. In clear river-water the wrought iron appears almost as resistant as cast iron, and certainly more so than the chilled metal.

5. When once the outer skin has been removed from cast iron it appears considerably more susceptible to corrosion. In behaviour it then more closely approximates to wrought iron. This is a point of considerable importance, and in laboratory tests careful note should always be taken of the surface of the metal prior to exposure to corroding influences.

6. Another point, which, however, is not indicated in the above table, is the interesting observation that those specimens which were 1 inch in thickness corroded very much less rapidly than those only 0·25 inch in thickness, but otherwise precisely the same. Reference has already been made to this (see p. 22), but the point is mentioned here by way of explanation of the fact that all Mallet's results are not summarised in Table XVII. Only those results obtained with cast iron of thickness 1 inch are given.[1]

If the above generalisations are accepted, the results in Table XVII. may be grouped together in another way of particular value to engineers. This has been done in Table XVIII.

TABLE XVIII.—*Mean Corrosion Factors of Cast and Wrought Iron as Calculated from Mallet's Data* (1840).

Metal.	Corrosion Factors.			
	Series I. Sea-water. 8° to 14·5° C.	Series II. Foul Sea-water. 8° to 14·5° C.	Series IV. Foul River-water. 2° to 16° C.	Series V. Clear River-water. 0° to 20° C.
Wrought iron . . .	100·0	118·6	68·8	12·3
Cast iron	63·6	20·5	40·4	0·9
Chilled cast iron . . .	64·4	63·1	51·2	12·9
Cast iron with skin removed .	77·6	127·8	64·4	23·5

[1] See also footnote, p. 39.

Series III. is omitted, as the conditions were artificial and therefore for the present purpose not strictly comparable.

Mallet calculated from his results that his standard wrought iron upon immersion in sea-water (Series I.) lost in weight at the rate of 20·56 lbs. avoirdupois per square foot of surface per 100 years. This is equivalent to a depth of corrosion of 0·543 inch (1·38 centimetres), assuming the corrosion to be uniform throughout. To determine the loss in weight experienced by any other of the metals under any of the above conditions it is only necessary to multiply these amounts by the corrosion factors of the metal as given in Table XVIII. and divide by 100. If the depth of corrosion rather than loss in weight is considered, this number must be again multiplied by the inverse ratio of the densities of cast and wrought iron.

This affords a means of checking, from practical experience, the correctness of the above conclusions. Thus, for example, Mallet [1] mentions that a number of cast-iron guns had been taken up from the wreck of the *Edgar*, which had lain in more or less foul sea-water for upwards of 129 years. The loss in weight due to corrosion was determined from the original specifications, which were known, as 32·81 lbs per square foot. Reference to Table XVIII. shows that the corrosion factor of cast iron with its skin removed (as in a bored cast-iron gun) is 127·8 in foul sea-water. Hence in 100 years it would lose 1·278 times as much as wrought iron in clear sea-water and corrode therefore to an extent of $20{\cdot}56 \times 1{\cdot}278$ lbs. per square foot. In 129 years the loss due to corrosion would be $1{\cdot}29 \times 20{\cdot}56 \times 1{\cdot}278 = 33{\cdot}90$ lbs. This is a remarkably close approximation to the loss actually found.

In 1843 Mallet [2] presented to the British Association a third and final report of his investigations. "The series of tables," he wrote, "is therefore now complete, and, I would venture to hope, present to the engineer sufficient data to enable him to predict the term of durability and allow for the loss by corrosion of iron in all conditions when entering into his structures. Their completion has involved no slight labour, having required more than five thousand accurate weighings to be made, without reference to other experiments."

[1] Mallet, *loc. cit.*, p. 238.
[2] Mallet, *British Association Reports*, 1843, p. 1.

The results given in this third report comprise those obtained by re-immersing the whole of the metals used in the previous research, and allowing them to remain under similar conditions to those already described for a further period of 732 days. In addition to these, "results are given of an entirely separate set of experiments on cast iron, wrought iron, and steel, exposed freely to the weather and to all the atmospheric influences at an altitude of about fifty feet above the surface in the city of Dublin."

The results are summarised in Table XIX.

TABLE XIX—*Summary of Results obtained by Mallet*, 1843, *all reduced to a common comparison for* 732 *days.*

Metal.	Corrosion Factors.				
	Series I. Sea-water.	Series II. Foul Sea-water.	Series III. Foul River-water.	Series IV. Clear River-water.	Series V. Air.
Wrought iron (standard) .	100·0	140·2	63·5	23·0	89·1
Calder hot-blast cast iron .	74·7	82·1	40·4	13·8	69·1
do. chilled . . .	82·0	116·0	41·7	12·5	46·2
Pentwyn hot-blast cast iron .	66·3	37·0	25·1	8·8	77·4
do. chilled . . .	101·8	117·9	34·3	12·2	31·5
Apedale hot-blast cast iron .	63·6	84·2	34·3	11·4	53·3
do. chilled . . .	78·4	11.1	21·4	7·2	4·5
Arigna cold-blast cast iron .	73·3	87·5	33·8	14·3	49·9
do. chilled . . .	81·7	67·5	32·1	10·7	15·3
Hardest cast iron procurable, chilled	53·9	38·6	28·5	10·4	31·5
Mixed Calder and Pentwyn .	70·2	125·0	36·7	9·0	75·0
Mixed Arigna and Pentwyn .	78·7	77·5	27·7	10·9	66·3
Cast iron, skin removed .	106·9	276·9	87·6	13·1	107·4

Mallet, in commenting on these results, directs attention to the reduced rate of corrosion of the cast irons as compared with their previous immersions. This he attributes to "the fact that the removal of metal by the corrosion of the previous immersion had bestowed a much more uniform or homogeneous surface upon all the specimens."

In a series of laboratory tests Mallet showed that if the corroded surface is not removed from the metal, corrosion proceeds at a uniform rate and is directly proportional to the time. Thus, he took six similar pieces of grey cast iron with planed surfaces,

and immersed them in sea-water slightly acidulated with hydrochloric acid and frequently renewed. One piece was cleaned and weighed every thirty days, the loss in weight giving a measure of the corrosion. The results are given in Table XX.

TABLE XX.—*Influence of Length of Exposure upon the Rate of Corrosion of Grey Cast Iron.* (*Mallet*, 1843.)

No.	Duration of Test. (Days.)	Loss in Weight. (Grains.)	Loss in Weight per 30 Days.
1	30	2·8	2·8
2	60	5·4	2·7
3	90	8·8	2·9
4	120	11·9	3·0
5	150	14·1	2·8
6	180	18·6	3·1

These results are confirmed by those of Heyn and Bauer (1910), which extended over seventeen months (see p. 52).

In general, the results detailed in Table XIX. resemble those in Table XVII., and similar conclusions may be drawn (see p. 39).

It is interesting to note, in connection with the aerial tests, that Mallet has considered the theory of the subject along very modern lines. He draws attention to the influence of rain and dew, to temperature, and to the effect of rise and fall of the barometer—which last factor appears to have been entirely overlooked until quite recently.

Discussing these results Mallet writes: "The numbers indicate that, in general, in moist air, chilled cast iron corrodes much more *slowly* than that cast in green sand; the contrary being, as before stated, the result in water. That the average loss on all varieties of cast iron in moist air is not much below that which takes place in clear sea-water in an equal time, and is much above that produced by clear fresh water in the same period. In the case of cast iron with the skin removed by planing, the loss in moist air is almost precisely the same as in clear sea-water,"

In 1880 Thwaite [1] collected together all available data, includ-

[1] Thwaite, *Journal of the Iron and Steel Institute*, 1880, No. II. p. 667.

ing those of Mallet already discussed, as to the relative corrodibilities of various forms of iron and steel under different conditions. His results are expressed as "coefficients of corrosion," that is, the loss in weight in grains experienced in twelve months by 1 square inch of the metallic surface. It is the relative values of these coefficients alone that are of interest at the present time; they have therefore been recalculated by the present author, taking steel as 100, and expressing all the other data relatively thereto.

TABLE XXI.—*Relative Corrodibilities of Steel, Wrought Iron, and Cast Iron in Neutral Media.* (*After Thwaite*, 1880.)

Metal.	Foul Sea-water.	Clear Sea-water.	Foul River-water.	Pure Air and Clear River-water.	City or Sea Air.
Steel	100	100	100	100	100
Wrought iron . .	101	113	127	97	100
Cast iron with skin .	34	65	34	89	39
Cast iron without skin .	119	92	64	87	71
Cast iron galvanised .	41	39	33	42	16

Despite the fact that the foregoing results were obtained from a variety of sources not strictly comparable with one another, several points are worthy of note. It will be observed that the steel and wrought iron, as at the present time, behave very similarly, save that in two cases the former possesses the advantage. In every case the cast iron, with its protective layer of "skin" or oxide, is superior to the two previous metals, whilst removal of the skin enhances its susceptibility to corrosion. Galvanising the metal improves its resistance, as, of course, is to be expected.

Reference must here be made to the experiments of Gruner,[1] who employed plates of steel and cast iron measuring 10 × 10 square centimetres in area and weighing some 350 grammes. The tests were conducted in air and in sea-water,[2] but in order to accelerate the former the plates were frequently dipped for a moment into dilute sulphuric acid. The analyses of the steels

[1] Gruner, *Annales des Mines*, 1883 (8), vol. iii. p. 5. A general summary is given in *Comptes rendus*, 1883, vol. xcvi. p. 195, but without numerical data.

[2] The tests in sulphuric acid solution are described later.

employed are given in Table XXII. and the corrosion results in Table XXIII.

TABLE XXII.—*Analyses of Steels used by Gruner* (1883).

No.	Carbon.	Manganese.	Sulphur.	Phosphorus.	Silicon.
1	0·160	0·140	0·048	0·039	0·093
2	0·450	0·160	0·044	0·037	0·139
3	0·600	0·150	0·022	0·034	0·186
4	0·800	0·140	0·027	0·034	0·279
5	0·900	0·110	0·025	0·033	0·186
6	1·400	0·110	0·033	0·030	0·372
7	1·560	0·120	0·020	0·032	0·320

The research will not bear comparison with that of Mallet in so far as manipulative skill and care are concerned. Not only was the work unduly hurried—the longest exposure being merely twenty days—but the method of weighing was not sufficiently

TABLE XXIII.—*Relative Corrosion of Steel and Cast Iron.* (*Gruner*, 1883.)

Metal.	Air Tests.				Sea-water. 9 Days.	
	5 Days.		20 Days.			
	Loss in Weight.[1]	Relative Corrosion.	Loss in Weight.	Relative Corrosion.	Loss in Weight.	Relative Corrosion.
Steel 1 . .	2·7	100	4·0	100	2·1	100
2 . .	3·0	111	4·3	108	2·0	95
3 . .	2·7	100	4·6	115	1·1	52
4 . .	2·5	93	4·8	120	2·2	105
5 . .	2·5	93	4·7	118	1·2	57
6 . .	1·5	56	4·4	110	2·0	95
7 . .	2·3	85	4·6	115	1·8	86
Cast iron 1 .	3·9	144	4·1	103	3·5	167
2 .	1·9	70	3·3	83	3·1	148
3 .	2·7	100	2·9	73	5·0	238
Spiegel .	2·8	104	1·9	48	7·0	333

refined in view of the small losses in weight experienced by the plates. The results, therefore, whilst not without interest and

[1] All losses in weight are expressed in grammes.

value, do not possess these features to the same extent as those of Mallet.

Analyses of the cast iron and spiegel are, unfortunately, not given in detail.

Cast iron I. was that used in the manufacture of Bessemer steel rails. High in graphite, 3 to 4 per cent. manganese, 1 to 2 per cent silicon. Low in sulphur and phosphorus.

Cast iron II. was from charcoal pig iron dating back to about 1845. Hard, compact; no analysis.

Cast iron III. was an ordinary grade of grey cast iron. No analysis.

Spiegel, containing from 20 to 25 per cent. manganese.

It will be observed that the cast irons and spiegel resisted atmospheric corrosion in the twenty days' test considerably better than the steels. In the sea-water tests, however, the steels showed to advantage.

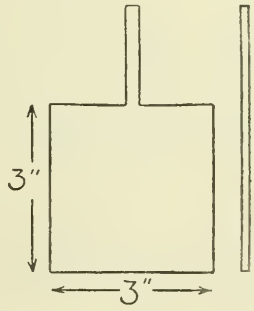


Fig. 4.—Plates used by Andrews (1885).

Very valuable data were published by Andrews[1] in 1885 on the relative corrodibilities of cast iron, steel, and wrought iron in sea-water. The plates of metal, measuring 3 × 3 inches in area and $\frac{1}{8}$ inch in thickness (see Fig. 4), possessing a total surface area of 19·5 square inches, were suspended vertically in sea-water in a wooden trough by means of their shanks from a wooden support above the sea-water. The latter was changed monthly during the 114 weeks of exposure, the losses entailed by

[1] Andrews, *Minutes of the Proceedings of the Institution of Civil Engineers*, 1885, vol. lxxxii. p. 281.

TABLE XXIV.—*Analyses and Losses in Weight of Plates of Wrought Iron, Steel, and Cast Iron upon Immersion in Sea-Water for* 110 *Weeks.* (*Andrews*, 1885.)

Metal.	Graphite.	Combined Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.	Loss in Weight. 56 Weeks. Grains.	Loss in Weight. 54 Weeks. Grains.	Total Loss in Weight.	Relative Corrosion.
Wrought iron I. . . .	...	trace	0·206	0·024	0·454	0·396	114·68	169·70	284·38	100·0
Wrought iron II. . . .	...	...	0·392	0·034	0·270	0·194	97·99	139·27	237·26	83·4
Soft Bessemer steel . .	...	0·150	0·015	0·111	0·064	0·540	108·85	158·18	267·03	93·8
Soft Siemens steel . . .	...	0·170	0·071	0·117	0·077	0·627	125·83	155·00	280·83	98·8
Soft cast steel . . .	...	0·460	0·074	0·025	0·210	0·184	148·65	227·74	376·39	132·4
Hard Bessemer steel . .	...	0·510	0·068	0·113	0·087	1·153	134·92	199·68	334·60	120·8
Hard Siemens steel . .	...	0·720	0·080	0·102	0·143	1·239	122·14	173·24	295·38	103·9
Hard cast steel . . .	...	1·407	0·121	0·056	0·080	0·360	139·57	184·54	324·11	114·0
Cast iron I.	1·500	2·010	0·410	0·250	0·450	0·650	160·62	254·25	414·87	145·9
Cast iron II.	2·620	0·670	1·940	0·090	0·950	0·520	182·70	172·73	355·43	125·0

evaporation in the interim being made good with distilled water. The analyses of the metals used and the results obtained in two sets of experiments of 56 and 54 weeks' duration respectively are given in Table XXIV.

Consideration of these results reveals several interesting points. The author draws " attention to the progressively increasing rate of corrosion of the plates during the periods stated, the increased corrosion during the second year compared with the first one, amounting in some instances to above 50 per cent." Generally speaking the cast irons have not resisted the sea-water as successfully as the wrought irons and low carbon steels, although there is little to choose between them and the 0·5 carbon steels. These results therefore are in fair accord with those of Gruner, but differ markedly from those of Mallet. The difficulty is that neither of the latter investigators has given analyses of his metals, so that it is impossible to determine exactly to what extent the results are comparable.

Andrews also carried out a few experiments with bars of iron and steel. These measured 0·75 centimetres in diameter and were suspended horizontally in separate glass vessels containing 7000 fluid grains of filtered sea-water from Filey Bay. The analyses of the metals used and the results obtained are given in Table XXV.

TABLE XXV.—*Analyses and Losses in Weight of Bars of Wrought Iron, Steel, and Cast Iron after Immersion in Sea-Water for Four Weeks.* (*Andrews*, 1885.)

	Graphite.	Combined Carbon.	Si.	S.	P.	Mn.	Percentage Loss by Corrosion.
Wrought iron .	...	...	0·224	0·000	0·239	0·071	0·22
Soft cast steel .	...	0·570	0·032	trace	0·066	0·147	0·27
Bessemer steel .	...	0·550	0·000	0·032	0·175	0·216	0·29
Hard cast steel .	...	1·600	0·145	0·002	0·025	0·183	0·35
Cast iron . .	2·400	1·000	0·570	0·140	0·580	0·860	0·38

The results support those already described as obtained with iron and steel in plate form.

In 1908 and 1910 Heyn and Bauer [1] gave the results of a very thorough investigation into the relative corrosion of three samples of steel, wrought iron, and cast iron on continuous immersion in distilled water. The metals were used in the form of plates and possessed the following dimensions and analyses :

TABLE XXVI.—*Dimensions and Analyses of Metals used by Heyn and Bauer* (1908–10).

Metal.	Length. Centimetres.	Breadth. Centimetres.	Thickness. Centimetres.	Total Area. Square Centimetres.
Steel	4·5	3·0	0·1	28·5
Wrought iron	4·5	3·0	0·05	27·75
Cast iron	4·5	3·0	0·3	31·5

	Steel.	Wrought Iron.	Cast Iron.
Carbon (combined)	0·04	0·08	0·62
Graphite	...	...	3·08
Silicon	0·01	0·017	2·40
Manganese	0·59	0·54	0·89
Phosphorus	0·034	0·15	0·663
Sulphur	0·025	0·032	0·09
Copper	0·162	0·204	0·074

A small hole drilled through each plate of the dimensions shown in Fig. 5 (*a*), allowed of suspension in a glass cylinder by means of a glass hook (Fig. 5, *b*). Each cylinder contained some 200 cubic centimetres of distilled water, and the top edge of the plate lay 3 centimetres below the surface of the water.

The plates were weighed prior to immersion, and after the desired period they were removed, rubbed clean, and again weighed, the loss in weight being taken as a measure of the corrosion.

All the experiments were carried out in quadruplicate, the mean actual losses in weight of the plates and their relative corrosions calculated for unit area [2] being given in the accompanying

[1] Heyn and Bauer, *Mitteilungen aus dem Königlichen Materialprüfungsamt*, Berlin, 1910, vol. xxviii. p. 62 ; 1908, vol. xxvi. p. 1.

[2] This correction is necessary in view of the fact, shown in Table XXVI., that the three sets of plates did not possess quite the superficial areas, these latter being in the following ratio—steel : wrought : cast = 1·000 : 0·974 : 1·105.

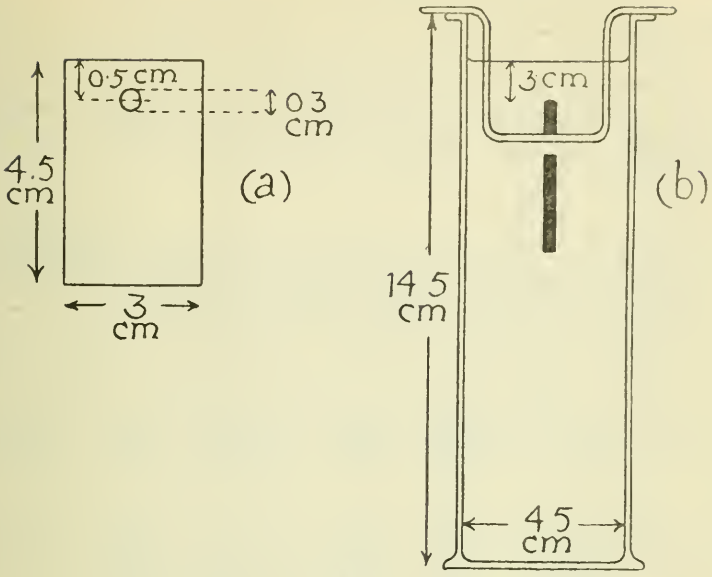


Fig. 5.—(*a*) Plates, and (*b*) Method of Suspension used by Heyn and Bauer (1908–10).

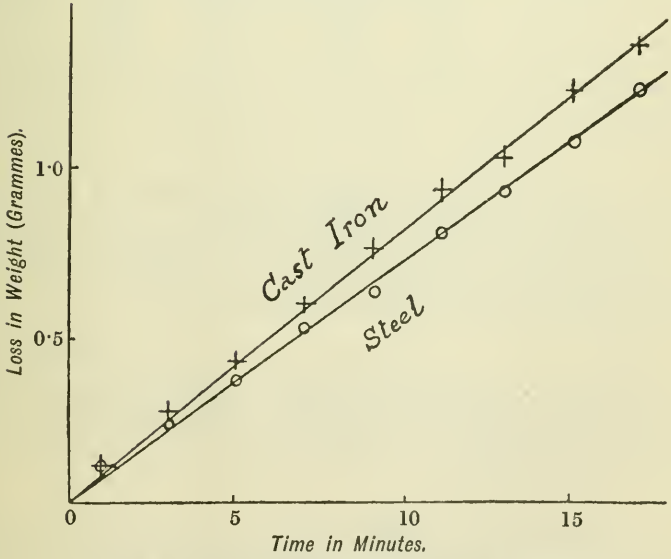


Fig. 6.—Rates of Corrosion of Cast Iron and Steel. (Heyn and Bauer, 1910.)

table, expressed relatively to that of the steel, which is taken as 100.

The experiments were conducted at the temperature of the room. No attempt was made to study the effects due to pitting, these being probably negligible under the conditions of the experiments.

TABLE XXVII.—*Losses in Weight of Plates of Steel, Wrought Iron, and Cast Iron upon Immersion in Water, and their Relative Corrodibilities per Unit Area.*[1] (*Heyn and Bauer*, 1910.)

Time. Months.	Steel.		Wrought Iron.		Cast Iron.	
	Loss in Weight. Grammes.	Relative Corrosion per Unit Area.	Loss in Weight. Grammes.	Relative Corrosion per Unit Area.	Loss in Weight. Grammes.	Relative Corrosion per Unit Area.
1	0·1016	100	0·0946	96·0	0·1034	92·5
3	0·2409	100	0·2397	102·5	0·2581	97·0
5	0·3689	100	0·3705	103·5	0·4152	102·0
7	0·5177	100	0·5202	103·5	0·5977	104·5
9	0·6247	100	0·6525	107·5	0·7589	110·0
1	0·8111	100	0·8002	101·5	0·9251	103·0
13	0·9417	100	0·9493	104·0	1·0497	100·5
15	1·0931	100	1·0635	100·0	1·2512	103·5
17	1·2654	100	1·1356	92·5	1·3875	99·5
Mean value	...	100	...	99·0	...	101·4

These results are shown diagrammatically in Fig. 6 for steel and cast iron. It will be observed that the rate of corrosion is, within the error of experiment, directly proportional to the time—exactly as Mallet showed for a shorter period with grey cast iron (see p. 44).

Another series of experiments,[2] which lasted twenty-two days, in which three liquid media were used, namely, distilled water, tap water, and a 1 per cent. solution of sodium chloride, yielded the following results:

[1] Mean results of four plates each.

[2] Heyn and Bauer, *op. cit.*, 1908, vol. xxvi. p. 32. These are not exactly the figures given by Heyn and Bauer, a slight correction having been introduced by the present author in view of the slight differences in area of the plates. See footnote, p. 50.

TABLE XXVIII.—*Relative Corrodibilities per Unit Area.*
(*Heyn and Bauer.*)

Liquid.	Steel.[1]	Wrought Iron.[1]	Cast Iron.[2]
Distilled water . . .	100	103·7	97·3
Tap water	100	104·8	93·2
1 per cent. NaCl[3] . . .	100	103·7	98·6

Some interesting experiments were carried out by Aston and Burgess[4] in 1910–1911. Twelve samples of metal were taken, mostly wrought iron and steel, but including one cast iron. For the present purpose it is sufficient to deal with those specimens only which had the same dimensions as, and were strictly comparable with, the cast iron.

The specimens measured $2 \times 1 \times 0{\cdot}5$ cubic inches. The cast-iron specimen was cut from a medium-grained grey iron casting. The analysis is not given, but the sample is claimed to be quite representative of iron casting in America. The surface skin had been removed before the tests were carried out.

In one set of experiments[5] the specimens were exposed to atmospheric corrosion on the roof of the Chemical Engineering Department at Wisconsin University. In the second set they were placed near a ventilator outlet on the roof of the same building, when the effect of weathering was supplemented by that of corrosive fumes. To avoid galvanic action the specimens were fixed into wooden racks. Their relative corrodibilities, as determined by loss in weight, are given in Table XXIX., the losses in weight of the open-hearth specimens being taken as 100 in each exposure set.[6]

[1] Means of four plates each. Analyses and dimensions as in Table XXVI.

[2] Means of two plates each. Analyses and dimensions as in Table XXVI.

[3] This concentration was chosen because previous experiments had shown it to be the most corrosive at ordinary temperatures—the critical concentration.

[4] Aston and Burgess, *International Congress of Applied Chemistry* (New York), 1912.

[5] The acid tests with these specimens are described on p. 67.

[6] The reader will understand that this is not the manner in which Aston and Burgess tabulate their results. The present author has recalculated them in this way in order to render them comparable with the other researches dealt with in this memoir.

TABLE XXIX.—*Relative Corrosion of Wrought Iron, Steel, and Cast Iron.* (*Aston and Burgess*, 1912.)

No.	Metal.	Atmospheric Corrosion.			Ventilator Corrosion.			Mean.
		75 Days.	150 Days.	300 Days.	75 Days.	150 Days.	300 Days	
1	Open-hearth high purity iron	100	100	100	100	100	100	100
5	Swedish wrought iron .	82·5	92	92	90	79	64	83
6	Open-hearth steel . .	97	88	124	94	85	59	91
11	Bessemer steel . . .	91	80	80	66	41	33	65
12	Medium-grained grey cast iron	113	69	117	80	55	36	78

The foregoing results speak for themselves. On the whole the cast iron compares very favourably with most of the other metals.

A unique feature of this research by Aston and Burgess lies in the fact that depth of pitting was also taken into account—for the first time, the present author believes, in so far as cast iron is concerned. The depth of pitting was determined by grinding down one surface of each specimen until the pit marks were just removed. The loss in weight thus experienced by the metal was determined. The total loss in weight, divided by the loss due to corrosion, is termed by the authors the *pitting factor*.

The following results were obtained in the case of the specimens exposed to atmospheric corrosion for 300 days.

TABLE XXX.—*Pitting Factors in Aston and Burgess's Experiments* (1912).

Metal No.	Loss in Weight through Corrosion. Grammes per Square Inch.	Total Loss in Weight through Grinding and Corrosion. Grammes per Square Inch.	Pitting Factor.
1. Open-hearth high purity iron	0·2193	1·0433	4·76
5. Swedish wrought iron . .	0·1995	0·9105	4·57
6. Open-hearth steel . .	0·2720	1·0220	3·76
11. Bessemer steel . . .	0·1756	0·9566	5·45
12. Cast iron	0·2530	0·8880	3·51

From the pitting point of view the cast iron shows to considerable advantage.

In the case of the ventilator specimens, however, the pitting was very much less for all the metals ; the superiority of the cast iron is not so evident. This is shown by the following brief summary :

	1.	5.	6.	11.	Cast Iron.
Pitting factor . . .	1·86	2·20	2·46	3·18	2·64

In 1915 Friend and Marshall[1] gave the results of an investigation of the relative corrodibilities of mild steel and cast iron. The specimens were in the form of rectangular blocks and measured $4 \cdot 5 \times 1 \times 1$ cubic centimetres. They were polished on an emery-wheel. In the tap and salt water tests the specimens were, after machining, laid on plates of paraffin wax in beakers containing 300 cubic centimetres of water and placed in a dark cupboard. Each beaker contained only one specimen. After three months the metals were removed, scraped clean, dried in a steam-oven and weighed, the loss in weight being taken as a measure of corrosion. In the alternate wet and dry tests the specimens were laid on paraffin (in the cold tests) or glass sheets (in the hot tests) in galvanised iron tanks fitted with a syphon arrangement whereby the metals were alternately submerged and exposed to air.

The analyses of the metals and the results obtained are given in the accompanying tables :

TABLE XXXI.—*Analyses of Metals used by Friend and Marshall* (1915).

	Steel.	Cast Iron.
Combined carbon . . .	0·21	0·61
Graphite	...	2·75
Silicon	0·013	1·72
Sulphur	0·026	0·085
Manganese	0·49	0·75
Phosphorus	0·053	1·06

[1] Friend and Marshall, *Journal of the Iron and Steel Institute*, 1915, No. I, p. 353.

TABLE XXXII.—*Relative Corrosion of Grey Cast Iron and Steel.* (*Friend and Marshall*, 1915.)

Corroding Medium.	Duration of Test.	Relative Corrosion.[1]	
		Steel.	Cast Iron.
Tap water	3 months	100	117
,,	,,	100	104
Salt water (3 per cent. NaCl)	,,	100	94
,, ,,	,,	100	90
Alternate wet and dry	2 ,,	100	81
,, ,,	3 ,,	100	100[2]
Alternate hot and cold	11 weeks	100	101
Alternate hot and cold, and wet and dry	6 ,,	100	71
Mean	...	100	95

Both in the salt-water tests and in the alternate wet and dry, the cast iron had the advantage. A 3 per cent. NaCl solution was taken, as representing a close approximation to sea-water. In the complete immersion tests in tap water, the steel appeared to prove slightly superior.

In a series of preliminary tests carried out with a large number of different commercial brands of iron and steel, the present author [3] has obtained the following results:

TABLE XXXIII.—*Relative Corrosion of Grey Cast Iron and Steel.* (*Friend*, 1922.)

	Complete Immersion in Tap-water. Months.	Alternate Wet and Dry. Months.	Complete Immersion in Artificial Sea-water. Months.	Mean.
Mean of nine samples of steel	104·5	193·8	85·7	100
Grey cast iron, CA	115·3	206·2	86·1	105·6
,, CC	110·2	209·6	94·2	107·8
,, W2	105·4	187·5	78·9	96·8

[1] Mean results of two tests each.
[2] Mean result of four tests.
[3] Friend, see Appendix. The skin had been removed from the cast iron.

b. Oxygen Absorption Methods.

One very obvious disadvantage of gravimetric methods of determining the rate of corrosion of iron lies in the impossibility of determining moment by moment how the corrosion proceeds. To a certain extent this difficulty is surmounted by experimenting with a considerable number of specimens under conditions as far as possible identical, and examining them one at a time at such different periods as may be desired. Owing to the well-known difficulty, however, of obtaining a series of exactly similar pieces of metal the results are often irregular.

One method by which a continuous record of the progress of corrosion might be registered without disturbing the system during the course of the experiment, consists in measuring volumetrically the oxygen absorption. When, however, it is remembered that iron rust invariably contains ferrous oxide in proportions that are not fixed, it becomes evident that unless the exact composition of the rust can be simultaneously determined the amount of iron attacked by a given volume of oxygen may vary by as much as 50 per cent. in two extreme experiments.

Thus, for example, suppose 33·6 litres of oxygen were absorbed and the iron were oxidised completely to hydrated ferric oxide, Fe_2O_3Aq, the amount of corroded metal would be 2×56 or 122 grammes (approximately). If, on the other hand, the conditions were such that the whole mass of rust consisted of hydrated ferrous oxide, FeOAq, then the weight of iron attacked would be $3 \times 56 = 168$ grammes, that is, 50 per cent. as much again.

These are extreme cases, but serve to show that, whilst the method may yield interesting results, and is particularly valuable on account of its yielding a continuous record, its limitations are very real. In an experiment carried out by the author[1] in 1911 a plate of wrought iron absorbed 50·16 cubic centimetres of oxygen in thirty-eight days, corresponding to the oxidation of

(*a*) 0·167 gramme of iron, assuming hydrated ferric oxide was produced; or
(*b*) 0·251 gramme of iron, assuming hydrated ferrous oxide resulted.

Actually 0·195 gramme of iron had been oxidised, 41·5 per cent. of which was present in the ferrous condition.

Whilst the proportions of ferrous iron in rusts obtained by

[1] Friend, *Carnegie Scholarship Memoirs*, 1911, vol. iii. p. 23.

corroding different samples of steel or wrought iron might not vary by more than a few per cent., the question is otherwise with cast iron. Owing to the lack of homogeneity of this metal, voltaic action is liable to be exceptionally pronounced, with the result that graphitisation occurs, the proportion of ferrous iron being exceptionally high. Cast iron, therefore, might show a

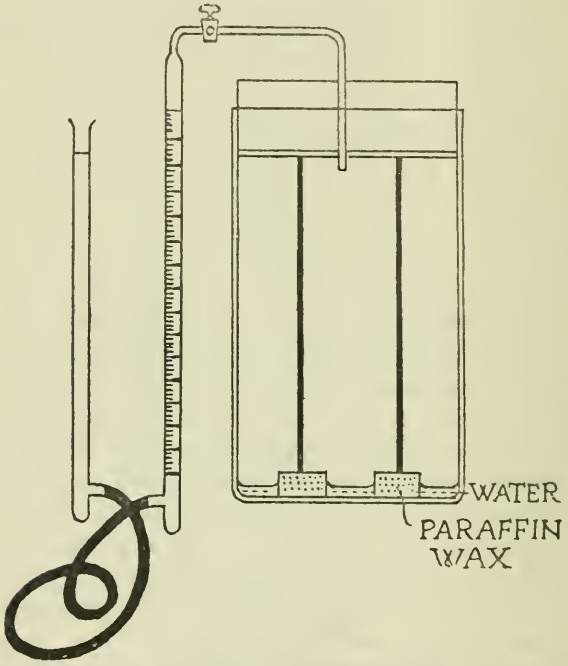


Fig. 7.—Arndt's Apparatus (1910).

distinctly smaller oxygen absorption, and yet be corroded more seriously than steel under test.

Having thus forewarned the reader, attention may be directed to a few researches in which the corrosion of cast iron has been studied by means of oxygen absorption.

One of the first investigators to use the oxygen absorption method was Kröhnke,[1] the gas being confined over mercury in a burette. His tests only lasted eighteen hours. Arndt[2] employed an apparatus similar to that depicted in Fig. 7.

[1] Kröhnke, *Metallröhren Industrie*, 1910 (April 10).
[2] Arndt, *Chemiker Zeitung*, 1910, vol. xxxiv. pp. 425, 1078.

Tubes of cast iron and steel, 20 centimetres long and 6 centimetres in external diameter, were placed, one each, in glass cylinders of two litres' capacity. The tubes rested upon paraffin blocks above a little water to keep the air moist. The apparatus was swept out with fresh air every two or three days in the later experiments, and the absorption continued for 122 days *in toto*. The analyses of the metals used and the results obtained are given in Tables XXXIV. and XXXV.

TABLE XXXIV.—*Analyses of Metals used by Arndt* (1910).

	Cast Iron.	Mild Steel.	Mannesmann Steel Tube.
Combined carbon . .	0·51	0·11	0·36
Graphite	3·01	...	...
Silicon	1·91	0·01	0·08
Manganese	0·57	0·34	0·39
Phosphorus . . .	1·30	0·03	0·10
Sulphur	0·13	0·06	0·07

TABLE XXXV.—*Absorption of Oxygen by Tubes of Steel and Cast Iron.* (*Expressed as Cubic Centimetres.*)

Time in Days.	Cast Iron Tube.	Mild Steel Tube.	Mannesmann Steel Tube.
3	39	42	80
5	58	82	143
10	83	168	269
20	128	327	441
40	195	525	642
70	286	731	870
122	416	949	1132

These results are very striking. The resistance offered by the cast iron to oxygen absorption accords well with its known resistance to atmospheric corrosion. Unfortunately Arndt gives no analyses of the rust obtained, so that there is no check upon his results.

In 1912 Arndt[1] published some further results obtained with different samples of cast iron of varying carbon content, but with the other elements, except perhaps phosphorus, reasonably con-

[1] Arndt, *Giesserei Zeitung*, 1912, vol. ix. pp. 461, 497.

stant. The results are expressed as curves, and it is difficult to trace any regularity between them and the composition of the metal. Indeed, it appears impossible to place any useful interpretation upon the results, particularly in view of the fact that

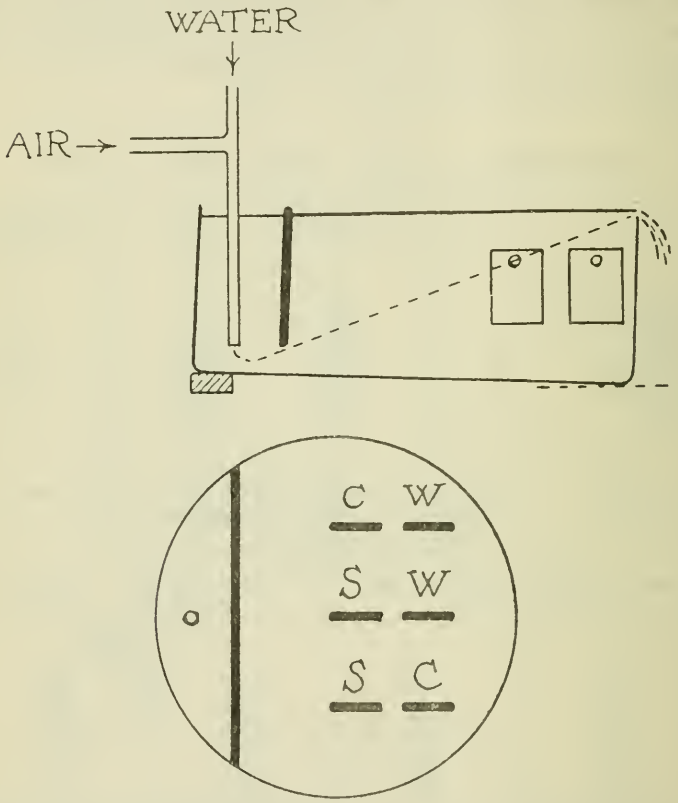


Fig. 8.—Iron Corroding in Moving Water. (Heyn and Bauer, 1910.)

Wölbling[1] does not confirm them in a research based on the same method. Unsupported by other evidence such as the composition of the rust formed, and failing a better method of ensuring an even distribution of moisture over the whole surface of the metal, the method appears to the present writer as of little value. Experiments carried out by this method, with the

[1] Wölbling, *Ferrum*, 1912, vol. x. p. 161.

specimens embedded in wet sand, lead to the conclusion that steel is more resistant than cast iron—the exact reverse of the results obtained in moist air.[1]

2. *Relative Corrodibilities of Steel, Wrought Iron, and Cast Iron in Neutral Corroding Media in Motion.*

Apparently the only recorded data concerning the influence of the rate of flow of water upon the corrosion of cast iron are those of Heyn and Bauer.[2] Several methods of experiment were adopted.

A. The first method consisted in suspending plates of steel, S, wrought iron, W, and cast iron, C, in a glass crystallising dish and allowing tap water and air to flow at a velocity of about 80 litres per hour through the system as shown in Fig. 8. The dish was slightly tilted so that the water passed under the baffle plate and escaped over the opposite edge of the dish. Blanks were carried out in a precisely similar manner with still water, the results being as follow:

TABLE XXXVI.—*Corrosion in Moving Water.*
(*Heyn and Bauer*, 1910.)

Metal. (Analyses and Dimensions, Table XXVI.)	Loss in Weight in Still Water at 16° to 17° C. Grammes. (Mean of 4.)	Loss in Weight in Moving Water at 13° C. Grammes. (Mean of 2.)	Relative Corrosion per Unit Area.	
			Still Water.	Moving Water.
Steel . . .	0·0992	0·1483	100	154
Wrought iron .	0·0904	0·1392	113	169
Cast iron . .	0·1110	0·2709	111	272

The steel and wrought iron appear to be equally affected, but the cast iron is considerably more affected by the movement of the water.

It should be remarked that the still-water tests are not strictly comparable with the moving-water tests, owing to the difference in temperature.

[1] Arndt, *Metallurgie*, 1911, vol. viii. p. 353. Wölbling, *loc. cit.*
[2] Heyn and Bauer, *loc. cit.*, 1910, vol. xxviii. pp. 93–102.

B. In a second method a rapid stream of tap water was made to flow down a glass tube into a large beaker of capacity 600 cubic centimetres, in which were suspended two metal plates similar to those already described (see p. 50). The arrangement is shown diagrammatically in Fig. 9.[1] The temperature ranged from 11° to 13° C. and the experiments lasted for twenty-two days, the results being as follow:

TABLE XXXVII.—*Corrosion of Steel and Cast-Iron Plates in Moving Water.* (*Heyn and Bauer*, 1910.)

Metal. (Analyses and Dimensions, Table XXVI.)	Velocity of Water in Litres per Hour.	Estimated[2] Velocity over Surface of Iron. Metres per Hour.	Losses in Weight of Steel Plates. Grammes.	Mean Losses. Grammes.	Relative Losses per Unit Area.[3]
Steel . .	0	0·00	0·0576 0·0556	0·0566	100
,, . .	15	3·25	0·1534 0·1180	0·1357	240
,, . .	50	10·85	0·0410 0·1242	0 0826	146
,, . .	350	75·95	0·0326 0·0428	0·0377	67
Cast iron .	0	0·00	0·0347 0·0353	0·0350	56
,, .	6·6	1·43	0·2989 0·2954	0·2971	475
,, .	36	7·81	0·2849 0·2976	0·2912	466
	240	52·08	0·1401 0·1540	0·1470	235

These results are shown graphically in Fig. 10. It will be observed that, as in the previous tests, the cast iron is much more affected than the steel by slight movement of the water. When the velocity of the water exceeds about 10 metres per hour, the rate of corrosion begins to show a decided reduction, and prolongation of the curves indicates that the corrosions would be reduced to a negligible quantity at approximately the following velocities:

Steel . . . . 250 metres per hour.
Cast iron . . . 160 ,, ,,

[1] Heyn and Bauer, *loc. cit.*, 1910, vol. xxviii. pp. 93–102.
[2] By the present author.
[3] Corrected by the present author. See footnote, p. 50.

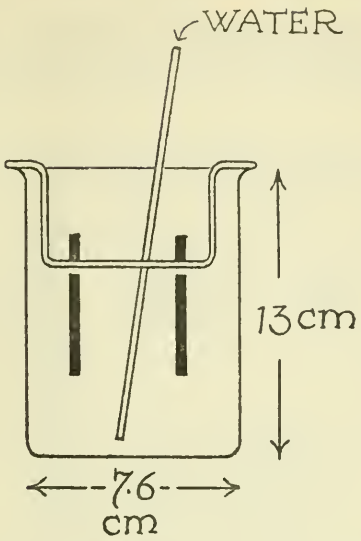


Fig. 9.—Iron Corroding in Moving Water. (Heyn and Bauer, 1910.)

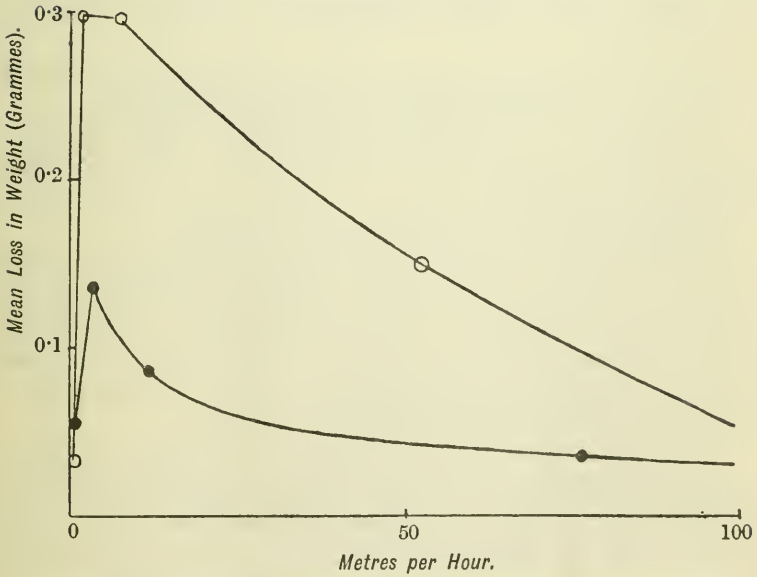


Fig. 10.—Influence of Rate of Movement of Water upon Corrosion. (Heyn and Bauer, 1910.)

Heyn and Bauer did not study this point, but the present author[1] has shown that, in the case of pure electrolytic iron foil, traces of rust alone appear at a water velocity of 3000 metres

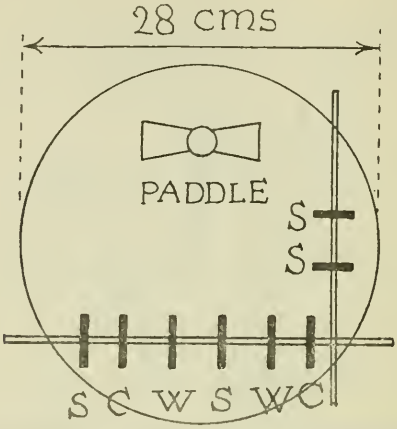


Fig. 11.—Iron Corroding in Moving Water. (Heyn and Bauer, 1910.)

per hour, whilst at about 10,000 metres no corrosion whatever can be observed.

The above methods of experiment are subject to several disadvantages, the more important of which are as follow:

1. Owing to the enormous quantities of liquid required, tests cannot be carried out with distilled water or other solutions of definite composition.

2. The temperature cannot be easily regulated.

3. The velocity of the water cannot be greatly increased, neither is it certain that both plates are exposed either equally or uniformly to the flow. Indeed, the discrepancies between the duplicates in the case of the steels at velocities of 15 and 50 litres per hour as given in Table XXXVII. suggest that the plates are not under precisely similar conditions.

C. The third method adopted by Heyn and Bauer consisted in suspending plates of steel, wrought iron, and cast iron by means of glass rods in a glass crystallising dish containing water or salt solution, and stirring the same by means of a wooden paddle,

[1] Friend, *Transactions of the Chemical Society*, 1921, vol. cxix. p. 932; *Transactions of the American Electrochemical Society*, 1921 (in the Press); see also Part V., p. 128.

which rotated at the rate of 120 revolutions per minute. The arrangement is shown in Fig. 11. The following results were obtained :

TABLE XXXVIII.—*Corrosion in Moving Water.*
(*Heyn and Bauer*, 1910.)

Duration of Experiments—22 days. Temperature—atmospheric.

Metal. (Analyses and Dimensions, Table XXVI.)	Liquid.	Number of Plates Tested.	Mean Relative Corrosion per Unit Area.
Steel	Tap water	4	100
Wrought iron . .	,,	2	119
Cast iron . . .	,,	2	153
Steel	1 per cent. NaCl.	2	596
Wrought iron . .	,,	2	583
Cast iron . . .	,,	2	574

As before, the cast iron is more affected by moving tap water than either the steel or wrought iron ; but in salt-water the metals behave very much alike.

This method possesses several advantages over those previously described. Thus the temperature and the nature of the corroding medium admit of control. On the other hand, the velocity of the water cannot be determined with accuracy, nor can its uniformity of movement over all the plates be guaranteed. As in the first set of experiments, therefore, there is no quantitative relation between the velocity of the water and rate of increase of corrosion.

3. *Relative Corrodibilities of Steel, Wrought Iron, and Cast Iron in Acid Media.*

In 1883 Gruner[1] gave the results of suspending plates of cast iron and steel in 0·5 per cent. sulphuric acid for several days. The analyses of the plates are given in Table XXII. The results obtained were as follows :

[1] Gruner, *Annales des Mines*, 1883 (8), vol. iii. p. 5.

TABLE XXXIX.—*Relative Corrosion of Cast Iron and Steel.* (*Gruner*, 1883.)

Metal.	Relative Corrosion.	
	3 Days.	10 Days.
Steel (mean results of 7 samples)	100	100
Cast iron, I.	2784	958
,, II.	140	312
,, III. . . .	1541	600
Spiegel (20 per cent. manganese)	263	104

The cast irons appear particularly susceptible to acid attack, whilst the spiegel, after ten days' immersion, has proved as resistant as the steels.

Experiments carried out by Heyn and Bauer in 1908 with dilute sulphuric acid (1 : 100) led to the following interesting results : [1]

TABLE XL.—*Relative Corrosion of Steel, Wrought Iron, and Cast Iron.* (*Heyn and Bauer*, 1908.)

Duration of Experiment. Hours.	Steel.[2]	Wrought Iron.[2]	Cast Iron.[2]
24	100	232	10,100
48	100	222	9,650

In 1912 Aston and Burgess [3] gave the results of exposing various samples of iron, steel, and cast iron to the action of 20 per cent. sulphuric acid for one hour. Twelve samples were taken, mostly wrought iron and steel, but including one cast iron. For the present purpose it is only necessary to discuss the results obtained with those specimens which had the same dimensions as, and were therefore more strictly comparable with, the cast iron.

[1] Heyn and Bauer, *ibid.*, 1908, vol. xxvi. p. 34. Each of the results represents the mean of four experiments.

[2] Analyses and dimensions as per Table XXVI.

[3] Aston and Burgess, *International Congress of Applied Chemistry*, 1912 (New York).

The specimens measured $2 \times 1 \times 0{\cdot}5$ cubic inches. The cast-iron specimens were cut from a medium-grained grey iron casting. The analysis is not given, but the sample is regarded as typical of that used in iron castings in America. The surface skin was removed prior to the testing. The specimens had previously been exposed (see p. 53) to atmospheric corrosion, or to corrosion by the atmosphere, supplemented by the effect of corrosive fumes from the laboratory ventilating shaft of the Chemical Engineering Department at Wisconsin University, but were ground and polished afresh.

The results are given in Table XLI.

TABLE XLI.—*Action of* 20 *per cent. Sulphuric Acid upon Specimens of Iron and Steel.* (*Aston and Burgess*, 1912.)

Metal.	Relative Corrosion of Specimens previously Exposed to Air.	Relative Corrosion of Specimens previously Exposed to Air and Fumes.
1. Open-hearth high purity iron .	100	140
5. Swedish wrought iron . .	320	361
6. Open-hearth steel . .	1960	2210
11. Bessemer steel . . .	2100	3170
12. Medium-grained cast iron .	3330	4080

The cast iron is seen to be the most severely attacked. It is interesting to note that the specimens that had previously been exposed to corrosive fumes were in every case more attacked than the others.

If reference be made to Table XXIX. it will be noted that the specimens most resistant to the ventilator corrosion proved most susceptible to acid attack.

In 1915 Friend and Marshall [1] determined the relative corrodibilities of mild steel and cast iron in various concentrations of sulphuric acid. The specimens were small rectangular bars, measured $4{\cdot}5 \times 1 \times 1$ centimetres and weighed approximately 30 grammes. After polishing on an emery-wheel they were weighed and laid on small paraffin wax sheets immersed in 300 cubic centimetres of acid, which, in the case of the two most dilute solutions, was frequently renewed. The analyses of the

[1] Friend and Marshall, *Journal of the Iron and Steel Institute*, 1915, No. I. p. 353.

metals are given in Table XXXI. The results obtained were as follow :

TABLE XLII.—*Relative Corrodibilities of Steel and Grey Cast Iron in Various Concentrations of Sulphuric Acid, at Room Temperatures.* (*Friend and Marshall*, 1915.)

Sulphuric Acid per Cent.	Duration of Test.	Relative Corrosion.[1]	
		Steel.	Cast Iron.
0·05	6 weeks	100	111
0·5	,,	100	119
5·0	3 hours	100	398
5·0	16 ,,	100	538
10·0	3 ,,	100	355
10·0	16 ,,	100	224
20·0	3 ,,	100	265

The cast iron is seen to be very inferior to the steel in its resistance to all concentrations of the acid. It is particularly noteworthy that the relative corrodibility of the cast iron fluctuates with the duration of the experiment. These results illustrate very forcibly the actually misleading nature of acceleration tests when used as a rapid means of determining the general corrodibility of iron and steel, as is sometimes done in commercial laboratories.

In a series of preliminary tests carried out by the present author [2] with 0·5 per cent. sulphuric acid over a period of twenty-two hours the following results have been obtained :

TABLE XLIII.—*Relative Corrodibilities of Steel and Grey Cast Iron in 0·5 per Cent. Sulphuric Acid.* (*Friend*, 1922.)

	Loss in Weight after 22 Hours. Grammes per Square Inch.	Relative Corrosion.
Mean of nine samples of commercial steels	0·2313	100
Grey cast iron, CA	1·3546	586
,, CC	1·3431	582
,, W2	1·2792	554

[1] Mean results of two tests each.

[2] Friend, see Appendix.

All these results agree in illustrating the susceptibility of grey cast iron to acid attack.

Other results, showing the relative rates of solution of grey cast iron and mild steel in progressively increasing concentrations of hydrochloric and sulphuric acids, have already been given (pp. 11, 12) and offer further confirmation.

Carbonic acid is, of course, an exceedingly weak acid ; nevertheless, according to the researches of Schleicher and Schultz,[1] cast iron is unable to withstand its corrosive action as efficiently as does wrought iron. Details of the method of experiments have unfortunately not been given. Presumably they were carried out at the room temperature and with due observance of the numerous precautions necessary for obtaining strictly comparable results.

The analyses of the metals employed are given in Table XLIV., and the corrodibilities expressed as percentage losses in weight, and also relatively to the wrought irons, are given in Table XLV.

TABLE XLIV.—*Analyses of Metals used by Schleicher and Schultz* (1908).

	Combined Carbon.	Graphite.	Si.	S.	Mn.	P.
Wrought iron, I. .	0·50	...	0·374	0·020	0·611	0·030
,, II. .	0·143	...	0·029	0·060	0·244	0·056
Cast iron, I. . .	0·66	3·05	1·410	0·020	0·475	0·384
,, II. . .	0·78	2·49	0·808	0·014	0·302	0·844

TABLE XLV.—*Relative Corrodibilities of Wrought Iron and Cast Iron in Carbonic Acid Solution.* (*Schleicher and Schultz*, 1908.)

Iron.	Carbonic Acid Solution in Air Absence.				Carbonic Acid Solution and Air.	
	Loss in Weight. Per Cent.	Relative Corrosion.	Loss in Weight. Per Cent.	Relative Corrosion.	Loss in Weight. Per Cent.	Relative Corrosion.
Wrought, I. .	0·11	100	...	...	0·27	100
,, II. .	0·12	109	0·27	100	...	...
Cast, I. . .	0·30	273	...	...	0·41	152
,, II. . .	0·31	282	0·37	137	...	...

[1] Schleicher and Schultz, *Stahl und Eisen*, 1908, vol. xxviii. p. 50.

Consideration of the foregoing data shows that in every case the cast iron was less resistant than the wrought metal.

Corrosion and Potential Difference.

It has long been known that when two different metals such as zinc and copper are partially immersed in a solution of an electrolyte, on connecting the unwetted portions with a wire an electric current passes. Thus, if the zinc and copper are immersed in dilute sulphuric acid a current passes from the latter to the former through the wire, the circuit being completed in the solution by passage of the current in the opposite direction.

Similar phenomena occur, although usually to a less well-marked extent, when two different pieces of iron are treated in an analogous manner. The direction in which the current flows depends upon a variety of factors such as the chemical composition of the metal, its physical condition and the nature of the electrolyte. The metal undergoing corrosion is termed the anode, and the current passes from it through the solution to the second metal —the cathode—and back to the former through the connecting wire. The present author has frequently observed that whilst strained or cold-worked iron is anodic towards portions of the same metal in an unstrained condition in dilute sulphuric acid, the contrary is usually the case in neutral corroding media, the strained portion being cathodic in dilute potassium chloride solution, for example. Clearly, therefore, the conditions under which electrochemical measurements are carried out must be clearly defined and carefully regulated.

In 1840 Mallet gave the results of a series of experiments in which white and grey cast irons were allowed to corrode both singly and in contact in sea-water. Mallet [1] found that the grey cast iron in contact with the white corroded with a greatly enhanced velocity, the white iron being largely protected. The total loss in weight of the connected plates, however, was greater than that experienced by the two plates separately. The results are given in Table XLVI., expressed relatively to the insulated white cast iron, the loss in weight of which is taken as 100.

[1] Mallet, *British Association Reports*, 1840, p. 266.

TABLE XLVI.—*Corrosion of Cast Iron in Sea-Water.* (*Mallet*, 1840.)

Metal.	Relative Corrosion in Sea-water after 25 Months.
White cast iron—alone	100
Grey cast iron—alone	143
White cast iron—in voltaic contact with Grey cast iron	38 429

One of the earliest researches to be carried out along these lines with wrought and cast irons was that of Andrews [1] who, in 1884, gave the results of an extensive series of investigations into the differences of potential manifested between pairs of various forms of iron when immersed in sea-water. It will suffice for present purposes to discuss the results only in so far as they concern cast iron and wrought iron, which latter metal was taken by Andrews as standard.

The method of experiment consisted in immersing sets of two bars of the metals in sea-water, the bars measuring 30 inches in length and 3 inches in diameter and fixed 0·5 inch apart. They were electrically connected with one another through a sensitive galvanometer. Each set comprised a wrought-iron bar and one cast-iron bar, and the experiments were continued for 300 days.

The analyses of the metals are given in Table XLVII.

TABLE XLVII.—*Analyses of Metals used by Andrews* (1884).

	Wrought Iron.	Cast Iron I.	Cast Iron II.
Graphite	...	2·780	2·620
Combined carbon	...	0·390	0·670
Silicon	0·392	2·340	1·940
Sulphur	0·034	0·090	0·090
Phosphorus	0·270	0·580	0·950
Manganese	0·194	0·450	0·520

The results obtained are given in Table XLVIII.

[1] Andrews, *Minutes of the Proceedings of the Institution of Civil Engineers*, 1884, vol. lxxvii. p. 323.

TABLE XLVIII.—*Potential Differences between Cast Iron and Wrought Iron in Sea-Water.* (*Andrews*, 1884.)

	Cast Iron I.	Cast Iron II.
Average potential difference (volts) between cast iron and wrought iron when former at higher potential (positive) . .	+0·030	+0·021
Highest potential difference observed whilst cast iron positive	+0·116	+0·092
Total number of days in which cast iron positive	233	246
Number of reversals of polarity . .	1	1
Average potential difference when cast iron negative to wrought iron . . .	−0·006	−0·003
Greatest potential difference observed whilst cast iron negative	−0·011	−0·005
Total number of days in which cast iron negative	66	53

A consideration of the foregoing results reveals the interesting fact that not only does the potential difference between the metals vary, but it may actually become reversed. Thus, for 233 days cast iron I. was at a higher potential, and hence less corrodible than wrought iron, whilst for 66 days it was at a lower potential, and hence more corrodible than the wrought metal. The total relative corrosion during the period is the sum of these two effects. The polarity changed but once. Andrews found, however, in the case of hard Bessemer steel when connected with wrought iron, no fewer than sixteen reversals or interchanges of polarity during 300 days.

When inquiry is made into the cause of these reversals, the problem is found to be very complex. The surface condition is mainly responsible for the electrical condition, and any protective, non-corrodible skin will tend to raise the potential and reduce corrosion. In neutral corroding media the rust usually adheres to some extent to the metal, and markedly influences the potential difference.

Finally, as the metal corrodes away, fresh surfaces become attacked, and if these vary slightly in composition or in physical condition, the potential difference must be proportionately affected. Hence with those metals where the initial potential difference

is but small, as in the case of ordinary wrought iron and steel, reversals will the more easily occur.

In 1885 Andrews[1] published further data. Having prepared series of plates of wrought and cast irons of the dimensions shown in Fig. 4, and having the compositions indicated in Table XXIV., the plates were suspended vertically, $\frac{5}{8}$ inch apart, in wooden troughs containing sea-water, and connected in pairs—one

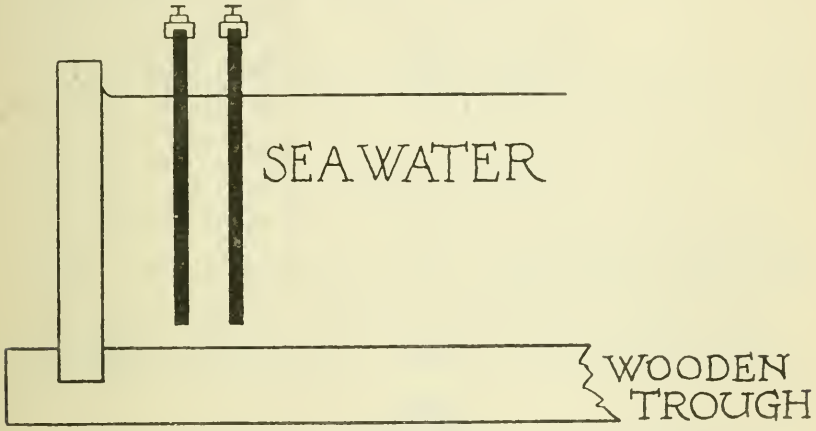


FIG. 12.—Corrosion of Cast and Wrought Irons in Contact in Sea-water. (Andrews, 1885.)

wrought to one cast iron—by brass screw clips attached to their shanks and joined by copper wire, as shown in Fig. 12.

The sea-water was changed monthly, any loss in the interim through evaporation being made good by addition of distilled water.

The losses in weight experienced by the plates during 110 weeks' exposure are given in Table XLIX., together with the losses experienced by exactly similar plates under precisely similar conditions, save that they were insulated instead of being galvanically connected.

During these tests a reversal of polarity was observed in each case, cast iron I. being at first cathodic and later anodic to the

[1] Andrews, *Minutes of the Proceedings of the Institution of Civil Engineers*, 1885, vol. lxxxii. p. 281.

wrought iron, whilst cast iron II. was first anodic and later cathodic.

It is interesting to note that the corrosion suffered by all the

TABLE XLIX.—*Losses in Weight of Plates of Wrought Iron and Cast Iron immersed in Sea-Water, both Singly and in Galvanic Connection, for* 110 *Weeks.* (*Andrews*, 1885.)

	Galvanically Connected.			Single Plates.[1]		
	Loss of Cast Iron. Grains.	Loss of Wrought Iron. Grains.	Total.	Loss of Cast Iron. Grains.	Loss of Wrought Iron.[2] Grains.	Total.
Cast iron I. . .	529·77	337·47	867·24	414·87	284·38	699·25
,, II. . .	450·53	385·19	835·72	355·43	237·26	592·69

plates when galvanically connected is appreciably greater than that of the insulated plates.

The results of a few tests carried out by Heyn and Bauer[3] were published in 1908 and, had it not been for the limitations

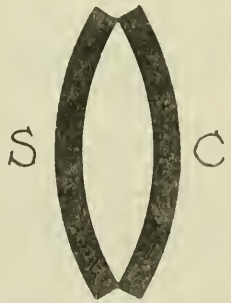


FIG. 13.—Corrosion of Steel and Cast Iron in Contact.
(Heyn and Bauer, 1908.)

due to the method of experiment, they would have been of particular interest in that they deal with the contact effect between

[1] See Table XXIV.

[2] It is not clear which of the wrought irons were used in these tests. The present author has assumed cast iron I. to have been coupled with wrought iron I., and cast II. with wrought II. But in any case it makes very little difference.

[3] Heyn and Bauer, *Mitteilungen Königlichen Materialprüfungsamt*, 1908, vol. xxvi. p. 23.

cast iron and steel not merely at room temperatures but also at 60° C. The samples of metal consisted of portions of piping (Fig. 13) which, in the case of the experiments at room temperature, were suspended in water both singly (in the case of steel) and in contact by the method shown in Fig. 5. In one series of experiments air was passed over the surface of the water by a similar arrangement to that shown in Fig. 2 ; in the second series air was bubbled through the water. The tests lasted for twenty-three days and yielded the following results : [1]

TABLE L.—*Corrosion of Steel and Cast Iron in Contact in Tap Water at Room Temperature.* (*Heyn and Bauer*, 1918.)

Condition of Experiment.	Losses in Weight of		
	Steel Alone. Grammes.	Steel and Cast Iron in Contact.	
		Grammes.	Grammes.
Air passed over . .	0·0787	0·0393	0·0424
Air bubbled through . .	0·1946	0·1426	0·1379

It is clear that the presence of the cast iron has reduced the corrosion of the steel, but it is very illogical to conclude, as Heyn and Bauer apparently do, that this reduction is due to galvanic protection afforded by the cast iron. It may be so in part ; indeed it probably is, for in a special series of experiments Heyn and Bauer found that the steel exhibited a higher potential than the cast iron, which is quite in accord with its reduced corrodibility. This cannot be the only cause, however ; it probably is not even the principal cause, for the method of experiment is unfortunate. In the contact tests the cast iron, lying as it does within the corrosion zone [2] of the steel, prevents a certain amount of oxygen from diffusing to the latter quite apart from any galvanic protection. The blank experiments with the steels alone, therefore, should, in order to be really comparable, have been carried out with cast iron close by but not actually in contact.

[1] All the data are the mean of two results.

[2] Friend, West, and Bentley, *Journal of the Iron and Steel Institute*, 1912, No. I. p. 259.

It is interesting to note that Mallet [1] in 1838 drew attention to a precisely similar error by one of his contemporaries in connection with supposed galvanic protection afforded to iron by contact with brass. The iron had apparently not corroded so freely purely because the brass had by its presence mechanically prevented access of oxygen.

No blank experiment with the cast irons alone appears to have been made by Heyn and Bauer, so that there is no means of judging whether or not the total corrosion is greater than the sum of the corrosions of the separate insulated metals. This would have been a clear indication of galvanic action. Andrews

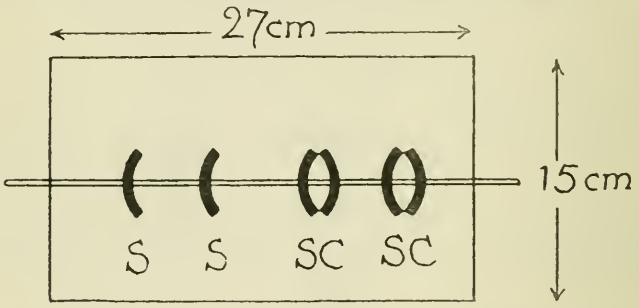


FIG. 14.—Corrosion of Steel and Cast Iron in Contact at Temperatures above Atmospheric. (Heyn and Bauer, 1908.)

found this to be the case in his experiments, but he also found both the cast iron and the wrought iron to be more corroded when in contact. But his metals were only connected by wire at the top, whereas in the experiments under discussion the steel and cast iron were in contact all down their edges, so that the protection afforded by the more corrodible metal would be proportionately more effective. On the other hand, the more corrodible metal would itself be proportionately more attacked, and for this reason it is particularly fortunate that no blanks were carried out.

The same criticism applies to the experiments at 60° C. These were carried out in enamelled troughs and arranged as shown in Fig. 14.

Tap water and water from two springs were used as corroding

[1] Mallet, *British Association Reports*, 1838, p. 299.

media, and the troughs were heated to 60° C. for seven hours daily and allowed to cool over night.

The results obtained are given in Table LI.

TABLE LI.—*Corrosion of Steel and Cast Iron in Contact in Water at Temperatures Varying from Atmospheric to 60° C.* (*Heyn and Bauer*, 1908.)

Condition.	Water.	Duration of Experiment. Days.	Loss in Weight of		
			Steel Alone.[1] Grammes.	Steel and Cast Iron in Contact.	
				Grammes.	Grammes.
Trough merely exposed to air .	Tap	24	0·2598	0·1904	0·3039
	Spring (1)	22	0·2461	0·2362	0·2878
	Spring (2)	22	0·2708	0·2431	0·2615
Air bubbled through trough . ..	Tap	24	0·2916	0·2518	0·2716
	Spring (1)	22	0·2670	0·2185	0·2651
	Spring (2)	22	0·2722	0·2104	0·2886

These results are similar to those obtained at room temperature. The method of experiment is open to the same objections, however, so that the results are inconclusive in so far as galvanic action is concerned. Analyses of the spring waters are also given, but it is not thought necessary to give them here.

There can be no doubt, however, that contact between steel and cast iron may in practice lead to increased corrosion and thereby become a source of danger.

In 1863 a serious accident occurred in Portsmouth Dockyard, where there was a large cast-iron salt-water tank, holding some 890 tons of water. The side of this tank gave way, and "an inspection of the broken parts of the tank disclosed the somewhat extraordinary fact that *the wrought-iron tie-rods in the interior of the tank were very much eaten away at their junction with the cast-iron plates*, where they had been submerged in the salt water."[2] Accidents of this character speak for themselves.

A few experiments were carried out by Heyn and Bauer with cast iron in contact with brass. In this case different liquid media

[1] Mean of two experiments each.

[2] *The Times*, June 19, 1863.

were employed, and the results thus derive an added interest (Table LII.). But unfortunately the method is faulty.

TABLE LII.—*Corrosion of Cast Iron in Contact with Brass in Various Media at Atmospheric Temperature.* (*Heyn and Bauer*, 1908.)

Duration of Experiments—one year.

Liquid.	Loss in Weight.		
	Cast Iron Alone. Grammes.	Cast Iron and Brass in Contact.	
		Grammes.	Grammes.
Distilled water . . .	0·9470	0·9782	0·0007
Glycerine and water (1 : 1) .	0·0621	0·0575	0·0007
Oil	slight gain	slight gain	0·0029

The brass does not appear to have exerted much influence ; but this is probably because the galvanic action is in the opposite direction, namely, tending to enhance the corrosion of the cast iron, whereas at the same time the brass is mechanically protecting the metal by preventing access of oxygen, as explained above. The total observed effect, therefore, is the algebraic sum of these two opposing actions. If anything, the cast iron in distilled water is very slightly more corroded when in contact with the brass. The enormous reduction in corrosion in the glycerine-water is noteworthy. The slight gain in weight in oil is probably due to absorption of the latter into the pores of the metal.

In water, of course, there is not the same opportunity for galvanic action to come into play as in solutions of electrolytes such as sodium chloride. It is not surprising, therefore, that in sea-water which contains approximately 3 per cent. of dissolved salt, brass should exert a more pronounced effect upon cast iron than in distilled water. Mention has already been made (see p. 8) of a case of rapid corrosion of cast iron in contact with copper of a vessel, the iron being corroded to a depth of half an inch during a sea voyage of less than five months' duration. E. Davy found that cast iron immersed in sea-water in contact with brass was rapidly attacked, and Mallet [1] concluded as the result of his own

[1] Mallet, *British Association Reports*, 1838, p. 299.

and of Davy's experiments "that brass or gun metal have no protective power over iron whatever, but, on the contrary, greatly promote its corrosion in sea or fresh water, and, as we also found, in diluted acids"—and this despite their zinc content.

Contact with metallic tin similarly accelerates the corrosion of iron in sea-water. This was first shown by Van Beck [1] and by Mulder [1] in 1837. Zinc, on the other hand, which is a more readily oxidisable metal than iron, protects the latter. This had been known for some time prior to 1834, but E. Davy [2] "has unquestionably the merit of having been the first to conduct a series of well-devised and careful experiments upon the subject on the large scale." This is now a well-recognised fact, as the extensive galvanising of iron articles carried out at the present time clearly indicates.

Results of Practical Experience of the Corrosion of Cast Iron in Service.

Although theories and laboratory tests may be of inestimable value in guiding the scientific and practical man alike, the final appeal must always rest with the behaviour of the metal in actual practice. It is most important, therefore, to collect and survey all such reliable practical evidence as is available, and correlate it with our theoretical and laboratory studies both for the purpose of drawing such general conclusions as may be serviceable in practice, and also as means of suggestion for future researches, with a view to filling the gaps in our knowledge.

In 1915 Messrs. Stewarts & Lloyds,[3] Limited, issued an interesting pamphlet dealing with the relative corrosion and value for pipe services of cast iron and steel. Emphasis is laid upon the different type of corrosion evidenced by steel from that to which cast iron is liable. In the case of steel pipes conducting soft water the internal "corrosion may attain a depth of $\frac{1}{8}$th of an inch, resulting in a nodular incrustation to a thickness of as much as an inch. Corrosion then practically ceases, the incrustation formed serving

[1] Quoted by Mallet, *loc. cit.*, p. 292.

[2] See Mallet, *loc. cit.*, p. 289; and referring to Davy's report, *ibid.*, *Transactions of the Sections*, 1835, pp. 34–35.

[3] See *The Iron and Coal Trades Review*, 1915, vol. xc. p. 215.

as an effectual preventive of further corrosion. In the case of cast iron the depth of corrosion may amount to $\frac{3}{8}$ths of an inch with nodular incrustation to a depth of 2 or 3 inches before further corrosion is arrested by the protection afforded. In either case when this nodular incrustation is removed, further corrosion occurs."

Attention is very usefully drawn to the fact that "the proportion of carbon in cast iron by volume (not by weight) is about 35 per cent. of the whole, whereas in steel it is only about 2 per cent. Any corrosion in steel is at once evident as pitting, but not so with cast iron. The fabric of carbon left on the surface of a cast-iron pipe so closely resembles cast iron in appearance that until a chisel is applied it may not be discovered that the pipe has corroded at all."

Discussing the Coolgardie steel pipe line it is pointed out that in those sections in which corrosion has taken place, "it has been found that the few castings employed, such as reducing pieces, valves, &c., have corroded very seriously—much more than the wrought-steel pipes. This is particularly noteworthy, because this pipe line has been actually cited by some engineers as a case in which cast iron should have been employed in preference to wrought steel. Those who are acquainted with the conditions are well aware that, had cast iron been used, not only would the cost of the scheme have been excessive, but almost certainly the corrosion in cast-iron pipes of the same size would have by this time so greatly increased the frictional resistance and consequent pumping costs on its 350 miles of length, as to render its further operation impracticable. This view is fully confirmed by the experience in the water-supply of Perth, Western Australia, which draws its water from the same source, and in which it has been found that a 12-inch cast-iron main has been reduced in capacity by about 75 per cent. in five years by internal corrosion and incrustation, while the 21-inch wrought-steel pipe laid beside it has proved practically free from corrosion after eleven years' use."

Cast Iron Pipes in France.

When the first pumping station connected with the Parisian water-supply was discontinued a few years ago, the cast-iron pipes

connecting with the Seine were taken up. They had been laid in 1802, and although they had seen over one hundred years of continuous service they were in such good condition that they might have been used over again. Their shape, however, was obsolete and they were remelted.[1]

A line of cast-iron pipes laid in 1748 in Clermont-Ferrand was still being worked in 1908,[2] despite their 160 years of service. Even older are the five lines of cast-iron pipes, 20 inches in diameter and 1000 feet long, which were laid in 1685 to convey the water to the fountains at Versailles. Very striking photographs, taken in 1909, are shown by McWane and Carson[3] of pieces of the pipes which, according to the official report, were "in apparently as good condition as when installed." Photographs are also reproduced of pieces of cast-iron and wrought-iron pipes used in the same service with each other for the same length of time. The cast iron appears little the worse for wear, whilst the wrought iron is completely destroyed.

Cast-Iron Pipes in Germany.

Jungst[4] mentions a curious case of corrosion of a cast-iron water-pipe line laid in 1894 for a length of some 1950 metres. Two years later, namely, in 1896, the pipe was laid bare in fifteen different places and found to have developed a large number of weak spots due to pitting. For a length of about 100 metres the pipe line was replaced by stouter cast-iron tubes. The pittings were apparently not due to faulty casting; they occurred at the top of the pipes lying in a line following the direction in which the pipes were laid. It was ascertained that the water in the pipes was only used intermittently, being at rest for about twenty hours each day, and in motion only four hours. The pitting was therefore due to the rising of air bubbles, which collected at the top of the water during the periods at which the latter remained stationary in the pipes.

[1] Gaines, *Transactions of the American Electrochemical Society*, 1908, vol. xiii. p. 55.

[2] And may be now, for all the present author knows to the contrary.

[3] McWane and Carson, *American Foundrymen's Association*, 1915, vol. xxiv. p. 593.

[4] Jüngst, *Stahl und Eisen*, 1899, vol. xix. p. 133.

Cast Iron in America.

In a most interesting account of the conduits used for conveying the domestic water-supply to Rochester, U.S.A., Gaines[1] discusses the relative durability of steel, wrought iron, and cast iron for this purpose. The water is drawn from Hemlock Lake, some twenty-nine miles south of the city, and conveyed by two conduits to the storage and distributing reservoirs. The older conduit, known as Conduit I., was constructed in 1873 to 1875, and is divided into five sections as follows :

Section.	Metal.	Length in Miles.	Diameter of Pipe. Inches.
1	Wrought iron . . .	10·0	36
2	Wrought iron . . .	0·3	24
3	Cast iron	5·75	24
4	Wrought iron . . .	2·63	24
5	Cast iron	8·75	24

Attention is drawn to the fact that no rust-holes have appeared in the cast-iron sections of the conduit during its thirty-two years of service, although leaks have occurred from time to time at the lead joints,[2] and tubercles forming on the interior walls have reduced the carrying capacity. No rust-holes, however, have appeared. A few leaks occurred in the wrought-iron sections and were repaired at intervals between 1894 and 1904. On the whole, Conduit I. is regarded as having given excellent service.

In 1894 a second auxiliary conduit was completed, known as Conduit II., consisting of 26 miles of steel pipe, 38 inches in diameter, and $\frac{1}{4}$ mile of cast-iron pipe 36 inches in diameter. From 1894 to 1900 the conduit was carefully inspected every summer on the outside and once or twice on the inside. It appeared to have remained in good condition all through the six years. In 1900, however, 2 leaks were discovered, in 1901 the number had risen to 15, and by 1907 no fewer than 164 leaks had been registered in the steel. In conclusion Gaines writes that experience " seems to show that cast iron resists corrosion better than any other form of iron."

[1] Gaines, *Transactions of the American Electrochemical Society*, 1908, vol. xiii. p. 55. Note conclusions, p. 93.

[2] A difficulty to which Gerhard directs attention. See p. 84.

In 1917 some useful information was published [1] concerning the life of cast-iron pipes in American railroad experience. Several instances of old installations were made the subject of careful examination on the Illinois Central Railroad, "with the result that the life of several of these has been accurately traced down to the present time. The most interesting of these is a pipe line laid at Centralia, Illinois, in 1855. This was a line of 4-inch cast-iron pipe approximately 10,000 feet long. After twelve years of service in 1867 the pipe line became inadequate for the water consumption, and upon examination it was found to be heavily encrusted. Efforts were made to improve its capacity by cleaning it and re-laying a part of it with clean-out boxes at intervals of 100 feet. This provided only a temporary relief, and the following year about 5000 feet of the line was taken up and relaid with 8-inch pipe, which is still in service after being in the ground forty-nine years.

"The 4-inch pipe relieved at Centralia was relaid in 1868 or 1869 at Ramsey, Illinois, where it remained in service until 1903, when it again became too small for the demand and was replaced by 6-inch pipe. Since that time the old 4-inch pipe has been used at various places, principally as drains."

"Some 6-inch cast-iron pipe laid at Centralia in 1868 and 1869 was taken up when the shops were abandoned in 1916. The pipe was found to be in such a good state of preservation after forty years of service that most of it was re-used, no distinction being made between the old pipe and the new cast-iron pipe."

"Another installation of which authentic records are available is one of 7500 feet of 4-inch cast-iron pipe at Little Wabash River, laid in 1857. This remained in service until July 1893, when it was replaced by larger pipe. The old pipe was stored at Centralia until 1894 or 1895, when portions of it were relaid at that place and at Effingham and at Big Muddy. The installations at the last-named places have since been removed, but the pipe at Centralia is still in service. No signs of paint can be found on the pipe at the present time, and apparently it never had been painted."

In June 1919 Gerhard [2] laid before the American Institute

[1] See *Iron Age*, 1917, vol. c. p. 167 (unsigned article).

[2] The following data are taken from a reprint of the paper circulated by Messrs. A. M. Byers Co., Pittsburgh, Pennsylvania. A general account of the work occurs in the *Journal of the Franklin Institute*, 1919, vol. clxxxvii. p. 99.

of Architects the results of an investigation carried out by him the previous year into the drainage system of some seventy-eight buildings in New York. Structures less than five years of age or smaller than six storeys in height were not examined. The buildings were as follows :

Age of Building.	Number Examined.
Over 30 years	13
25 to 30 ,,	10
20 to 25 ,,	17
15 to 20 ,,	17
10 to 15 ,,	15
5 to 10 ,,	6

Of these, 28 were drained by cast-iron piping; 1 with black wrought iron; 3 mixed black steel and wrought iron; 12 galvanised steel; 14 galvanised wrought iron; and 20 mixed galvanised-steel and wrought-iron piping.

Examination was confined to cellar sewers and roof vent pipes, of which latter 1676 were inspected. In describing the results of the investigation Gerhard writes :

" The three different materials used for vent pipes showed two distinct forms of corrosion or rusting. The cast-iron pipes and also nearly all the wrought-iron pipes were *pitted* or pockmarked, usually to a shallow depth, and the thickness of the pipe showed but a slight reduction. The steel pipes, on the other hand, exhibited a characteristic flaking or scaling. When these scales, the products of corrosion, are removed—and usually it is easy to do so by hand—there is often only a thin pipe shell left."

The paper is illustrated by several very clear and beautiful photographs which show " the surprisingly good condition of the cast-iron vents—some from thirty-five to fifty years old—the excellent showing made by the genuine wrought-iron pipe, even after twenty-seven years, and the inferior and very often extremely bad condition of the steel vents when in service twenty years or more.

" The chief defect of the cast-iron piping is its lead-caulked joint, which is not to be trusted as a permanent one, wherever large quantities of either hot water or steam pass through the pipes. Another objection, as is well known, is the greatly increased number of joints, which involve more labour in the erection and in the supporting of the stack pipes.

"The investigation showed conclusively that, in point of durability and liability to corrosion, steel pipe is inferior to both cast-iron and genuine wrought-iron pipe. Incidentally it appeared that the galvanising coating is less of a protection against rust on steel than on wrought-iron pipes, and that usually it begins to disappear when steel pipe has been in service from ten to twenty years."

It is of interest to note that some practical rules laid down by the American Foundrymen's Association for obtaining cast irons resistant to corrosion are in substance as follow[1]:

1. Use white iron if possible. White irons are particularly useful where any acidity is to be encountered (see p. 28).
2. If it is not practicable to use white iron castings, chill those surfaces which are destined to come into contact with corroding media.
3. If grey iron must be used, render the castings as dense and close-grained as possible by the use of steel scrap or otherwise.
4. Use pig irons of good quality, coupled with good cupola practice. Avoid oxidised metal, and if possible employ deoxidising agents, as, for example, titanium or vanadium.
5. Keep the sulphur content as low as possible (see p. 25).

[1] Gaines, *Iron Age*, 1913, vol. xc. p. 1358.

PART II.

THE PROTECTION OF IRON WITH PAINT AGAINST SUBAQUEOUS CORROSION.

The author has frequently drawn attention to the important differences between atmospheric and subaqueous corrosions. It was to be anticipated, therefore, that the conditions under which a coat of paint affords a maximum protection to iron exposed to atmospheric corrosion will not necessarily be identical with those requisite when the metal is continuously submerged under water.

In a series of papers[1] results have already been given of several hundred field tests in which plates of mild steel were exposed under various conditions to the atmosphere for periods ranging from several months to five years. The object of the present research was to determine the general principles underlying the conditions necessary for the preservation of iron continuously submerged in water, and to compare and contrast these with the results already obtained for aerial corrosion.

Method of Experiment.

It was at first intended to employ large plates of mild steel similar to those used in aerial corrosion, but a difficulty lay in obtaining the use of a sufficiently large tank or reservoir in which the conditions would remain sufficiently uniform throughout the entire mass of the water. Iron, when completely immersed in water, is astonishingly susceptible to slight movement in the water and variation in temperature. Added to this is the well-known difficulty of obtaining any two sheets of the metal that will corrode at precisely the same rate even when placed under identical external conditions.

It was eventually decided, therefore, to use small plates

[1] Friend, *Carnegie Scholarship Memoirs*, 1912, vol. iv. p. 1 ; 1913, vol. v. p. 1 ; 1918, vol. x. p. 77 ; *Journal of the Iron and Steel Institute*, 1921, No. I. p. 365.

of metal. These were selected of two grades, namely, 24 and 30 B.W.G., cut into squares 10 × 10 centimetres in area, and weighing (when cleaned) approximately 50 and 25 grammes respectively. The plates were made of mild open-hearth steel, closely similar to those used in the previous researches,[1] and containing about 0·1 per cent. of carbon. They were used in one of two conditions :

1. Exactly as they arrived from the mills with the coating of scale upon them. The surfaces were very smooth and enabled an even coat of paint to be applied.

2. The plates were freed from scale by immersion in dilute sulphuric acid. They were then removed, washed, and soaked in dilute caustic soda solution to neutralise any acid remaining in the pores of the metal.[2] After again washing, the plates were polished with emery-paper. Plates treated in this manner are referred to as " pickled " in the sequel.

The various paint mixtures were made by thoroughly mixing together the different ingredients in a mortar. The pigments were dried at 100° C. prior to weighing, in order to obviate irregularities due to absorbed moisture. The oils employed in this research were as follows :

No. 2.—Pure Baltic raw linseed oil.
4.—Oil No. 2, heated 36 hours at about 300° C. in air absence. No drier.
5.—Oil No. 2, heated 42 hours at about 300° C. in air absence. No drier.
11.—Pure Calcutta raw linseed oil, heated 4 hours at 270° C. No drier.
12.—Sample of commercial boiled oil, with drier.

The plates were weighed before and after painting, and when the paint had set were placed in tanks filled with tap water. Various devices were adopted for maintaining the plates in nearly vertical positions, care being taken that their resting points should always be against glass or preferably paraffin wax and never against metal, as otherwise disturbing effects due to galvanic action might ensue.

After the exposure had been sufficiently prolonged, the plates were soaked in caustic soda solution to remove the paint, washed, dried, and any rust removed by gentle scraping and with emery-paper. They were then weighed, the loss in weight being taken as a quantitative measure of corrosion, and hence of the pro-

[1] For analyses see Friend, *Carnegie Scholarship Memoirs*, 1918, vol. x. p. 85.
[2] Friend, *Transactions of the Chemical Society*, 1912, vol. ci. p. 50.

tection afforded by the paint. Full particulars of all the experiments are given in the Table of Results, pp. 100–102.

The Relative Proportions of Oil and Pigment.

The influence of varying the relative proportions of oil and pigment upon the protective properties of paint may be studied in three ways, namely :

A. *Employing the same Weight of Pigment.*

The effect is well shown by the data in Table I. The plates were coated with 50 per cent. and 60 per cent. deep Indian Red paints respectively and exposed to corrosion for ten months. Whilst the weight of pigment, namely 0·300 gramme on each side, or 5·5 lbs. per 100 square yards, was constant, in Series VII. the amount of oil was 50 per cent. greater than in Series IX.

Table I.

Series.	Composition of Paint by Weight.	Grammes of D.I. Red on each side.	Grammes of Oil on each Side.	Mean Loss in Weight. Grammes.
VII.	50 D.I. Red 50 Oil No. 11	0·300	0·300	0·631
IX.	60 D.I. Red 40 Oil No. 11	0·300	0·200	0·584

The mean corrosion in Series VII. is nearly 10 per cent. greater than in Series IX. In contradistinction, therefore, to the results obtained with aerial corrosion, by increasing the amount of oil but keeping the weight of pigment constant, there is a decided decrease in efficiency.

B. *Employing the same Weight of Oil.*

By keeping the amount of oil constant and increasing the quantity of pigment the protection afforded is at first increased. A maximum efficiency, however, is reached with equal amounts of pigment and oil, after which further increase in pigment

causes a marked reduction in protection. This is clearly shown by the results detailed in Table III. and shown graphically in Fig. 1.

C. *Employing the same Weight of Paint.*

This method yields analogous results to the preceding, as is evident from the following data :

TABLE II.

Weight of paint on each side—0·400 gramme, or 7·3 lbs. per 100 square yards.
Length of exposure—10 months.

Series.	Pigment (D.I. Red). Per Cent.	Weight of Oil each Side. Grammes.	Weight of Pigment each Side. Grammes.	Mean Loss in Weight. Grammes.
I.	30	0·280	0·120	0·653
III.	40	0·240	0·160	0·553
V.	50	0·200	0·200	**0·440**
VIII.	60	0·160	0·240	0·514
X.	70	0·120	0·280	0·557
XII.	80	0·080	0·320	0·530

Here again the maximum protection is afforded by the 50 per cent. paint. Different oils and pigments will no doubt yield different optimum mixtures. The best results appear to be obtained when the proportion of oil is just sufficiently high to yield a mixture possessing smooth working properties under the brush.

FUNCTIONS OF A PIGMENT.

The chief functions of a pigment, other than decorative, are to afford mechanical support to the linoxyn and to reduce the permeability of the paint. By increasing the amount of pigment, therefore, and keeping the linoxyn constant, greater protection against corrosion should be afforded. There must be a limit, however, to the amount of pigment which a given weight of oil can bind efficiently, and when once this limit has been passed, further addition of pigment will reduce the protective power. That such is the case is well demonstrated by the results in the following table :

TABLE III.

Weight of oil on each side—0·200 gramme, or 3·7 lbs. per 100 square yards.
Length of exposure—10 months.

Series.	Weight of D.I. Red on each Side. Grammes.	Per Cent. D.I. Red in Paint.	Total Weight of Paint in Lbs. per 100 Square Yards.	Mean Loss in Weight due to Corrosion. Grammes.	Relative Corrosion.
II.	0·086	30	5·2	0·534	121
IV.	0·133	40	6·1	0·463	105
V.	0·200	50	7·3	**0·440**	**100**
IX.	0·300	60	9·2	0·584	133
XI.	0·467	70	12·2	0·832	189
XIII.	0·800	80	18·3	0·843	192

and shown diagrammatically in Fig. 1.

Consideration of the foregoing results shows that, as theory would demand, the addition of pigment at first reduces the cor-

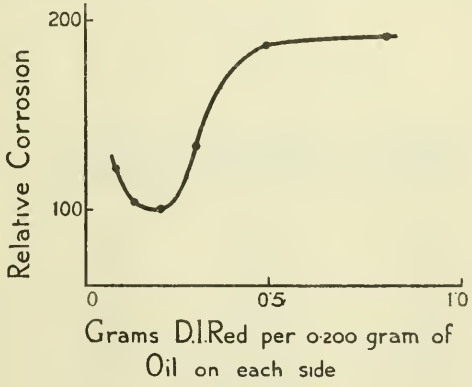


FIG. 1.

rosion, an optimum mixture being obtained with equal weights of oil and pigment. The proportions necessary to produce optimum mixtures will no doubt vary for oils and pigments. It is interesting to note that closely similar results were obtained in the series of experiments on aerial corrosion (*loc. cit.*, p. 91), the optimum percentage of ferric oxide being in that case about 60 per cent.

The Relative Values of Thin, Thick, and Multiple Coats of Paint.

It was shown by the author [1] in 1913 that iron corrodes more seriously when coated with thick layers of paint and continuously immersed in water for several months, than when covered with thin coats of the same paint and treated in a similar manner. This result, so different from what one might expect, and so opposed to that obtained in the case of aerial corrosion, has now been confirmed. This is evident from a consideration of the data given in Table IV., strictly analogous results being obtained with varying amounts of ferric oxide and linseed oil, ranging from 30 to 80 per cent. of the pigment. There can be no doubt, therefore, that the observation applies generally for subaqueous corrosion and is not merely a coincidence for one particular mixture.

Table IV.

Length of exposure—10 months.

Series No.	Per Cent. of Pigment in Paint.	Weight of Paint on each Side of Plate. Grammes.	Weight of Paint in Lbs. per 100 Square Yards.	Loss in Weight of Plates due to Corrosion. Grammes.
I.	30	0·400	7·3	0·653
II.	30	0·286	5·2	0·534
III.	40	0·400	7·3	0·553
IV.	40	0·333	6·1	0·463
VII.	50	0·600 (2 coats)	11·0	0·631
V.	50	0·400	7·3	0·440
IX.	60	0·500	9·2	0·584
VIII.	60	0·400	7·3	0·514
XI.	70	0·667	12·2	0·832
X.	70	0·400	7·3	0·557
XIII.	80	1·000	18·3	0·843
XII.	80	0·400	7·3	0·530

[1] Friend, *Carnegie Scholarship Memoirs*, 1913, vol. v. p. 1.

In connection with the above table it is interesting to note that the plates in Series VII. received two coats of paint, namely one of 0·400 gramme (7·3 lbs. per 100 square yards) directly comparable with that on the plates in Series V., followed by one of 0·200 gramme (3·7 lbs. per 100 square yards). It thus appears that the second coat of paint is not merely a waste of labour

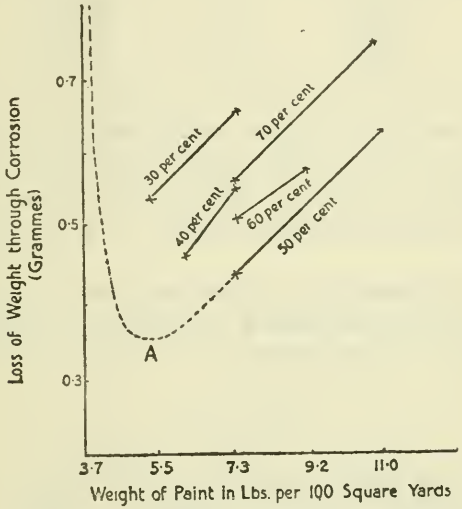


Fig. 2.

and good material, but is actually detrimental to the efficiency of the first coat.

When these results are represented graphically, as in Fig. 2, the curves obtained are approximately parallel. If continued backwards the 50 per cent. cuts the abscissa at the zero point, suggesting that if there were no paint there would be no corrosion. This is clearly impossible, for unprotected iron corrodes much more rapidly than the painted metal. There must therefore be a minimum point for each curve, at which thickness the paint offers a maximum protection, as indicated at A in the case of the 50 per cent. paint.

An attempt was therefore made to determine the position of A by coating series of plates with very thin layers of paint. The results are summarised in Table V.

TABLE V.

Paint used—50 per cent. D.I. Red. Duration of exposure—5½ months.

Series.	Weight of Paint on each Side. Grammes.	Weight of Paint in Lbs. per 100 Square Yards.	Mean Loss in Weight. Grammes.	Relative Corrosion.
XIX.	0·000	nil	4·174	100
XX.	0·095	1·7	2·745	66
XXI.	0·235	4·5	0·695	17
XXII.	0·503	9·2	0·451	11

When these results are considered in conjunction with those in Table IV. it is evident that a maximum protection is afforded in the case of the 50 per cent. paint by a coating of 0·4 to 0·5 gramme per square decimetre, that is, 7 to 9 lbs. per 100 square yards.

A few experiments were also carried out with coats of linseed oil alone of varying thicknesses and without any pigments. The results are detailed in Table VI.

TABLE VI.

Series.	Weight of Linseed Oil on each Side. Grammes.	Weight of Oil in Lbs. per 100 Square Yards.	Length of Exposure. Months.	Mean Loss in Weight. Grammes.	Relative Corrosion.
XIV.	nil	nil	2	0·9756	100
	0·0590	1·0	2	0·2080	21·3
	0·1235	2·2	2	0·1270	13·0
XIX.	nil	nil	5½	4·174	100
XV.	0·043	0·7	5½	3·488	84
XVI.	0·120	2·2	5½	1·263	30
XVII.	0·250	4·6	5½	1·165	28
XVIII.	0·500 (2 coats)	9·2	5½	0·968	23

As there was great danger of crinkling, it was not desirable to spread more than about 0·25 gramme of oil (*i.e.* 4·6 lbs. per 100 square yards) on any one plate at once. Two coats of oil were therefore applied in Series XVIII., each of 0·250 gramme. The second coat crinkled badly but did not appear to injure the underlying first coat.

It is evident that by increasing the thickness of the linseed oil coat even to the point at which crinkling occurs, namely, 9·2 lbs. per square yard, the metal is progressively protected against corrosion. The plates in Series XV. were all perforated in numerous places with rust pits which had eaten right through the metal. The corrosion, therefore, was economically much more serious than that suffered by the unprotected plate (Series XIX.), which, although it had lost a greater weight of metal, had corroded uniformly over its entire surface.

Mention may here be made of the work of Liebreich and Spitzer who, in 1912,[1] observed that, in a series of acceleration tests in which painted iron plates were kept in boiling water for ninety-six hours, the tendency of the metal to corrode was increased by increasing the number of coats of paint. Four coats were found to give distinctly less favourable results than one single thin coat.

The authors explained their results on electrochemical grounds, according to which the boundary between the iron and its coat of paint contains hollows and prominences, which may be microscopic in size in the case of well-polished surfaces. The hollows become filled with water either by absorption from without or as the result of decomposition of linseed oil or linoxyn, which are known to evolve water during oxidation. This water serves to connect electrically the metallic iron and pigment, the former becoming anodic to the latter. The iron thus readily corrodes. Mathematical arguments are adduced to show that the thicker the coat of paint, the greater is the tendency of the metal to corrode.

It is difficult to believe, however, that this can be the correct explanation for the following reasons.

Liebreich and Spitzer conclude, in pursuance of their theory, that without doubt (*zweifelsohne*) it may be regarded as a general axiom (*ganz allgemein gültig*) that corrosion increases with the number of coats of paint. The German words are enclosed in brackets to show how emphatic the authors are. The present author has already shown, however, that in aerial corrosion multiple coats of paint and even single thick coats protect the

[1] Liebreich and Spitzer, *Zeitschrift für Elektrochemie*, 1912, vol. xviii. p. 94; *Revue de Métallurgie*, 1912, vol. ix. pp. 1, 78, 160, 275.

metal more efficiently than one thinner coat. Further, in subaqueous corrosion it has now been shown that, unless a coat of paint exceeds a certain thickness, the thicker the coat the greater is the protection afforded.

The explanation of the protective action of paint appears to lie in the retarding effect of the colloidal "vehicle."[1] The author has already directed attention to the inhibiting action of even dilute solutions of colloids, and not merely upon corrosion but upon chemical and physical reactions in general which involve a change of state.[2] The added pigment on the one hand tends to retard corrosion by increasing the hardness and impermeability of the paint, but by its electrochemical action, on the other hand, it tends to stimulate corrosion. The final effect of the paint, therefore, is the algebraic sum of these three tendencies.

Effect of Heat Treatment of the Oil.

If linoxyn were perfectly impervious to moisture, and did not gradually disintegrate owing to slow oxidation, paint would yield a very permanent protection for iron and steel against corrosion. The problem therefore arises as to whether or not it is possible to so treat linseed oil that upon setting the resulting film of linoxyn shall possess the minimum porosity and the maximum resistance to chemical disintegration. To a certain extent this can be done by heating linseed oil in the absence of air when it polymerises, yielding a thicker, litho oil.

Some Raw Baltic oil was therefore treated in this manner for the author by Dr. Morrell of Messrs: Mander Bros., and in Table VII. are given the physical constants of the treated oils.

Tests carried out with these oils showed that the more prolonged the heating, the greater the extent of polymerisation, and the more thoroughly did paint made from them protect iron from atmospheric corrosion.[3] It was of interest, therefore, to determine if the same holds true for subaqueous corrosion. The results of the experiments carried out with this end in view are given in Table VIII.

[1] Friend, *Transactions of the Chemical Society*, 1921, vol. cxix. p. 932.
[2] Friend and Vallance, *ibid.*, 1922, vol. cxxi. p. 466.
[3] Friend, *Carnegie Scholarship Memoirs*, vol. x. p. 77.

TABLE VII.

	Density at 15° C.	Relative Viscosity.	Molecular Weight.	Relative Permeability to Moisture.[1]
Oil No. 2—Raw Baltic . .	0·9337	100	740	100
Oil No. 4—Same oil heated 36 hours at 300° C. . . .	0·9476	459	1000	79
Oil No. 5—Same oil heated 42 hours at 300° C. . . .	0·9626	3770	1420	35

TABLE VIII.

Weight of paint on each side—0·307 gramme, or 5·6 lbs. per 100 square yards.
Length of exposure—5 months.

Series.	Composition of Paint.	Mean Loss due to Corrosion. Grammes.	Relative Corrosion.	Relative Corrosion in Aerial Tests.[2]
XXIII.	50 D.I. Red 50 Oil No. 2	0·423	100	100
XXIV.	50 D.I. Red 50 Oil No. 4	0·365	86	56
XXV.	50 D.I. Red 50 Oil No. 5	0·120	29	31

The greater protective efficiencies of the polymerised oils are very pronounced, the results closely resembling those previously obtained in aerial corrosion tests.

STANDARD PAINT.

From the foregoing it is evident that a standard paint is required, against which all preservative coatings for iron shall be tested under standard conditions. Until this is done there is no possible means of comparing the relative efficiencies of the numerous paints now on the market.

[1] The permeability to moisture was determined by the method described by the author, *Carnegie Scholarship Memoirs*, 1911, vol. iii. p. 1.

[2] Friend, *Ibid.*, 1918, vol. x. p. 77.

It is obviously desirable that the standard paint shall possess as few constituents as possible, and these easily obtainable on different occasions in similar states of purity and physical condition.

From the foregoing experiments it would appear that such a standard might consist of a polymerised oil prepared in a well-defined manner from a pure grade of linseed oil, without the addition of a drier, and mixed with a certain percentage of some form of anhydrous ferric oxide pigment, such as Venetian red or Indian red. It might be diluted, when necessary, with a volatile hydrocarbon which, upon evaporation, would leave no solid residue. The same weight of this mixture (namely oil and pigment, not including turpentine) should be applied to each square yard of surface tested as in the case of the preservative paint to be compared with it, and the metal surfaces so painted exposed to corrosion under identical conditions.

Much more research is necessary before it will be possible to state the precise nature and treatment of the oil and pigments to be employed and their relative proportions, and experiments are in progress with this object in view.

The Influence of Mill Scale.

It is a matter of common knowledge that when iron leaves the mills it is coated with scale or oxide, which adheres very tenaciously to its surface. So long as this covering remains intact it affords a very efficient protection against corrosion; but if for any reason it is rendered discontinuous the exposed portions of the underlying metal rapidly rust and corrosion continues underneath adjacent layers of scale, which now begin to peel off. If the metal has been painted, the paint will tend to peel off with the scale. Many painters therefore prefer to remove all scale before painting. This may be done by pickling, sandblasting, or even by simple weathering. In this latter case the metal is allowed to rust until corrosion has proceeded to a sufficient extent to loosen the scale. The whole is then thoroughly scraped and the metal given its first coat of paint. All these processes, however, are a source of loss, for not only do they entail labour, but they involve wastage of a certain amount of good metal.

The author has already shown that, in the case of iron and steel structures exposed to aerial corrosion, the most economical procedure is to apply the paint whilst the scale is still on, but after any loosely adherent flakes and rust have been removed.[1] It seemed important, therefore, to ascertain whether or not the same procedure was advisable in the case of iron destined for exposure to complete immersion in water.

Ten plates were taken, five being pickled whilst five were allowed to retain their coat of scale. All were coated with 0·400 gramme (*i.e.* 7·3 lbs. per 100 square yards) of 50 per cent. D.I. Red paint and exposed to corrosion in the usual way. The results were as follow :

TABLE IX.

Paint used—50 per cent. D.I. Red. Length of exposure—10 months.
Weight of paint on each side—0·400 gramme, or 7·3 lbs. per 100 square yards.

Series.	Surface of Plate.	Mean Loss in Weight.	Relative Corrosion.	Relative Corrosion in Aerial Tests.[2]
V.	Pickled	0·440	100	100
VI.	With scale still on	0·391	89	54

The advantage is seen to be most distinctly with the plates from which the scale had not been removed, a result closely similar to that obtained in aerial corrosion. The superiority of the oxidised plates was in reality considerably greater than the above figures indicate, because the loss in weight of the pickled plates is entirely due to corrosion, whereas the loss experienced by the oxidised plates is that due to loosened scale as well as to the oxidation of the iron itself.

It would appear, therefore, that—

The cheapest method, and one best calculated to prolong the economic life of the metal, lies in painting steel structures whilst their scale is still on, after first removing any loosely adhering flakes and rust.

The coat of paint will last rather longer than if applied to

[1] Friend, *loc. cit.*, p. 114.
[2] Friend, *loc. cit.*, p. 114. The results for ten months' aerial exposure.

the pickled surface, and the labour and time involved in removing the scale are saved.

When the coat of paint is worn out or disintegrated it should be scraped off, together with any rust and loosened scale, and the structure painted afresh in the ordinary manner.

Table of Results.

(All weighings are expressed in grammes.)

Series.	Surface of Plate.	Composition of Paint by Weight.	Mean Weights of Paint on each Side.	Exposure to Water. Months.	Plate No.	Loss in Weight.	Mean Loss.
I.	Pickled	30 D.I. Red 70 Oil No. 11	0·400	10	21 22 23 24 25	0·728 0·655 0·612 0·757 0·550	0·653
II.	,,	30 D.I. Red 70 Oil No. 11	0·286	10	26 27 28	0·452 0·655 0·495	0·534
III.	,,	40 D.I. Red 60 Oil No. 11	0·400	10	31 32 33 34 35	0·597 0·590 0·590 0·462 0·525	0·553
IV.	,,	40 D.I. Red 60 Oil No. 11	0·333	10	36 37 38	0·585 0·372 0·431	0·463
V.	,,	50 D.I. Red 50 Oil No. 11	0·400	10	1 2 3 4 5	0·425 0·412 0·372 0·454 0·537	0·440
VI.	With scale on	50 D.I. Red 50 Oil No. 11	0·400	10	11 12 13 14 15	0·507 0·391 0·372 0·345 0·340	0·391
VII.	Pickled	50 D.I. Red 50 Oil No. 11	1st coat: 0·400 2nd coat: 0·200	10	6 7 8 9 10	0·597 0·483 0·665 0·772 0·687	0·631

TABLE OF RESULTS—(*continued*).

Series.	Surface of Plate.	Composition of Paint by Weight	Mean Weights of Paint on each Side.	Exposure to Water. Months.	Plate No.	Loss in Weight.	Mean Loss.
VIII.	,,	60 D.I. Red 40 Oil No. 11	0·400	10	46 47 48 49 50	0·412 0·490 0·443 0·572 0·653	0·514
IX.	,,	60 D.I. Red 40 Oil No. 11	0·500	10	43 44 45	0·730 0·451 0·572	0·584
X.	,,	70 D.I. Red 30 Oil No. 11	0·400	10	51 52 53 54 55	0·848 0·575 0·435 0·453 0·472	0·557
XI.	,,	70 D.I. Red 30 Oil No. 11	0·667	10	56 57 58	0·834 0·808 0·853	0·832
XII.	,,	80 D.I. Red 20 Oil No. 11	0·400	10	41	0·530	0·530
XIII.	,,	80 D.I. Red 20 Oil No. 11	1·000	10	42	0·843	0·843
XIV.	,,	No oil Oil No. 4 Oil No. 4	0·000 0·1235 0·0590	2 2 2	60 61 62	0·9756 0·1270 0·2080	0·9756 0·1270 0·2080
XV.	,,	Oil No. 12	0·043	5½	69 70 71	3·367 3·496 3·602	3·488
XVI.	,,	Oil No. 12	0·120	5½	72 73 74	1·162 1·338 1·288	1·263
XVII.	,,	Oil No. 12	0·250	5½	75 76 77	1·072 1·048 1·295	1·165
XVIII.	,,	Oil No. 12	1st coat: 0·250 2nd coat: 0·250	5½	78 79 80	0·958 0·938 1·008	0·968
XIX.	,,	No paint	...	5½	81	4·174	4·174

TABLE OF RESULTS—(*continued*).

Series.	Surface of Plate.	Composition of Paint by Weight.	Mean Weights of Paint on each side.	Exposure to Water. Months.	Plate No.	Loss in Weight.	Mean Loss.
XX.	,,	50 D.I. Red 50 Oil No. 12	0·095	5½	82 83 84	2·612 2·882 2·742	2·745
XXI.	,,	50 D.I. Red 50 Oil No. 12	0·235	5½	85 86 87	0·841 0·729 0·514	0·695
XXII.	,,	50 D.I. Red 50 Oil No. 12	0·503	5½	88 89 90	0·510 0·432 0·412	0·451
XXIII.	,,	50 D.I. Red 50 Oil No. 2	0·307	5	91 92 93	0·410 0·372 0·498	0·423
XXIV.	,,	50 D.I. Red 50 Oil No. 4	0·307	5	94 95 96	0·490 0·297 0·308	0·365
XXV.	,,	50 D.I. Red 50 Oil No. 5	0·307	5	97 98 99	0·069 0·154 0·136	0·120

PART III.

THE INFLUENCE OF STRAIN UPON THE CORROSION OF IRON.

The influence of strain upon the rate of corrosion of iron and steel is a problem that has not been investigated as thoroughly as its importance would warrant. In 1894 Andrews [1] published an account of experiments in which various pieces of iron and steel were subjected to tension, torsion, and flexion. They were then immersed together with pieces of the unstrained metals in a saturated solution of common salt, and in every case it was found that the strained metal was cathodic to the unstrained, and hence less readily corroded. These results were supported by Walker and Dill [2] in 1907, but exactly opposite results were obtained by Hambuechen [3] and by Burgess,[4] the strained iron being anodic to the unstrained and hence more readily attacked.

The present author has carried out similar tests and obtained results analogous to those of all the previous investigators, the strained metal sometimes functioning as cathode, and at other times as anode. The explanation appears to be as follows :

Barus [5] concludes, as the result of studying the distribution of energy absorbed in rupturing a piece of iron, that " as much as one-half of the work done in stretching up to the limit of rupture may be stored up permanently." It seems reasonable to suppose, therefore, that this energy will be liberated when the metal is oxidised ; in other words, the metal will be attacked more readily, its potential rising with increasing strain. This is precisely what is found to occur in acid media. Burgess observed

[1] Andrews, *Minutes of the Proceedings of the Institution of Civil Engineers*, 1894, vol. cxviii. p. 356.

[2] Walker and Dill, *Transactions of the American Electrochemical Society*, 1907, vol. xi. p. 153.

[3] Hambuechen, *Bulletin, University of Wisconsin, Engineering Series* 8, 1900.

[4] Burgess, *Transactions of the American Electrochemical Society*, 1908, vol. xiii. p. 17.

[5] Barus, *United States Geological Survey, Bulletin No.* 94, 1892.

it with dilute hydrochloric acid and Hambuechen with ferric chloride—a readily hydrolysable salt. The present author finds this to be the case not only in dilute sulphuric acid but also in concentrated solutions of potassium alum. In both of these cases the metal passes into solution without rusting in the ordinary acceptation of the term.

A new theory of corrosion [1] has recently been offered, according to which ordinary rusting is in the main an entirely different phenomenon from chemical solution. When iron rusts in a neutral medium such, for example, as an aqueous solution of potassium chloride, chemical solution does take place to a certain very limited extent, but if corrosion depended upon this reaction alone it would be relatively small. The true cause of corrosion under these conditions lies in the formation of colloidal iron hydroxide which catalytically assists in the oxidation of the iron, being alternately oxidised by the air and reduced in contact with the metal. This catalytic action explains why moist rust is so corrosive towards iron, and why corrosion, when once initiated, proceeds readily. Now it does not follow that, because a state of strain facilitates the rate of solution of the metal, it will also facilitate the catalytic oxidation of the metal by colloidal iron hydroxide. Indeed there are reasons for believing that a slight *retardation* of catalysis might occur, and this would explain the observations of Andrews, who used saturated sodium chloride solution as electrolyte, and of the present author, who employed dilute solutions of very pure potassium chloride, that in such media the strained metal is usually cathodic to the unstrained. The potential difference is admittedly small,[2] but it is the algebraic sum of two effects, namely :

(i) That due to chemical solution acting in one direction, and

(ii) That due to retarded catalysis acting in the other direction —two effects that nearly balance each other, effect (ii) being normally slightly the greater.

Now if the electrolyte is not quite pure, or if the iron contains a little sulphur or other substance that will facilitate the chemical

[1] Friend, *Transactions of the Chemical Society*, 1921, vol. cxix. p. 932. See also Part V.

[2] Walker and Dill, *loc. cit.*; Richards and Behr, *Publications of the Carnegie Institute, Washington*, 1906; *Zeitschrift für physikalische Chemie*, 1907, vol. lviii p. 301.

solution, so that effect (i) is enhanced, a reversal of polarity may occur. This would explain the reversal observed by Hambuechen when using common salt and frequently found by the present author with different electrolytes. In hydrolysed salts, such as ferric chloride, effect (i) is greatly increased, and results comparable in magnitude with those obtained with dilute acid may be anticipated. Hambuechen found such to be the case experimentally.

All of these measurements, however, depend upon the surface conditions of the metals. In acid solution, if the metal is uniformly strained or unstrained throughout, the effects may continue fairly constant until most of the metal has dissolved, because the dissolved metal diffuses away leaving the surface free. Hence in acid solutions, determination of the differences of potential between strained and unstrained metals may be expected to give comparable results with those obtained by determination of the rate of solution by methods of weighing after more prolonged exposure—assuming, of course, that the metals are chemically and physically uniform throughout their mass.

As will be seen later, experiment shows that in acid solutions strained iron dissolves with appreciably greater velocity than the unstrained metal, as electrochemical measurements indicate.

Indirect support for these views is found in the fact, observed by the author, that stainless and high-nickel steels, whilst almost incorrodible in the normal condition, are relatively very much more corroded when strained, although the actual amount of corrosion may still be small. Presumably the alloying element prevents the formation of the catalyst, so that such corrosion as does occur is due to solution, and this increases, as has been shown, with strain.

In the case of corrosion of ordinary steels in neutral solution, however, whilst the initial potential differences may be very definite, they are liable to be disturbed by accumulations of rust on the metallic surface with consequent acceleration or retardation of corrosion according to circumstances. Hence reversals of polarity may easily occur, and for this reason the electrochemical data are of little value for the determination of the relative resistances of the metals towards corrosion over prolonged periods. As no

reliable quantitative data appear to have been published, the present research has been undertaken with a view to throwing further light upon this important problem.

Material Used.

The steels used in this research were obtained as cylindrical bars, 1 inch in diameter, and in four grades, namely A, B, C, D, which differed mainly in their carbon content. From each bar three pieces were cut (denoted in the sequel as A, AA, AAA ; B, BB, BBB, &c.), 9 inches long, and ground into test-bars of the shape shown in Fig. 1 for the A, B, C, and D pieces. The

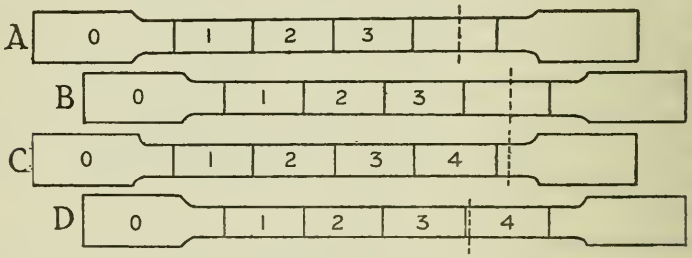


Fig. 1.

figure also shows by broken lines the places at which the bars snapped. Small marks were made along the length of each bar exactly 1 inch apart, and the steels were then placed in a tensile testing machine and broken.[1] The total and sectional elongations were noted, the bars turned to a uniform diameter, sawn at the marks into small cylindrical pieces, approximately 0·8 inch in height, and 0·6 inch in diameter. The exact size of each test-piece was measured, and its superficial area exposed to corrosion was calculated.[2] It is assumed that the portion of the metal under the grips was not appreciably strained.

[1] The author's thanks are due to Mr. J. Lloyd Bentley, who analysed the metals ; to Mr. C. W. Marshall, who ground the test-pieces to shape ; and to Mr. S. H. Moorfield, M.Sc., under whose supervision the bars were broken.

[2] As the differences in the superficial areas were very small, amounting on the average to about 2 per cent., the extremes being about 3·5 per cent. either way from the mean, it is assumed that the rates of corrosion are directly proportional to the areas. It is only when the areas vary by large amounts that this proportionality becomes appreciably incorrect.

TABLE I.—*Analysis of the Steels.*

	A.	B.	C.	D.
Carbon	0·174	0·467	0·920	1·350
Silicon	0·132	0·150	0·076	0·092
Manganese . . .	0·600	0·480	0·706	0·286
Sulphur	0·033	0·051	0·024	0·024
Phosphorus . . .	0·033	0·044	0·030	0·027

Physical Data.

Test-Bar.	Carbon per Cent.	Yield Point. Tons per Square Inch.	Mean Yield Point.	Ultimate Stress. Tons per Square Inch.	Mean Ultimate Stress.	Total Elongation per Cent.	Mean Elongation per Cent.
A	0·174	24·3		34·8		25·4	
AA		26·9	26·3	34·4	34·6	27·7	27·6
AAA		27·6		34·7		29·6	
B	0·467	29·4		44·9		18·0	
BB		28·4	29·7	44·7	45·0	14·8	17·3
BBB		31·2		45·3		19·1	
C	0·920	45·1		59·9		5·5	
CC		35·4	39·4	65·1	62·8	9·0	7·0
CCC		37·8		63·3		6·6	
D	1·350	41·0		58·8		2·3	
DD		38·2	39·6	57·6	58·2	1·6	2·1
DDD		39·7		58·2		2·3	

DENSITIES.

The densities of the test-pieces were determined in the usual manner by weighing in air and in air-free water with the results given in Table II.

The density falls with rise of carbon, as usual. The influence of strain also in the main tends to slightly reduce the density, as has been shown to be the case with the pure metal.[1] In some cases the effect is rendered inappreciable (the D pieces) or even

[1] Kahlbaum and Sturm, *Zeitschrift für anorganische Chemie*, 1905, vol. xlvi. p. 217. See also Lowry and Parker, *Transactions of the Chemical Society*, 1915, vol. cvii. p. 1005.

negatived (the B pieces) by irregularity in the test-pieces themselves.

TABLE II.

Mean Temperature, 16° C.

Test-Piece.	Carbon Content per Cent.	Elongation per Cent.	Density.	Mean Density.
AA 0	0·174	0	7·8624	7·8606
AAA 0		0	7·8588	
AA 2		17·2	7·8612	
AAA 2		17·2	7·8590	7·8584
AA 3		34·3	7·8562	
AAA 3		42·2	7·8570	
BB 0	0·467	0	7·8425	7·8458
BBB 0		0	7·8490	
BB 2		9·4	7·8479	
BB 3		10·9	7·8512	
BBB 2		12·5	7·8429	7·8474
BBB 1		17·2	7·8444	
BBB 4		29·7	7·8505	
CC 0	0·920	0	7·8437	7·8427
CCC 0		0	7·8416	
CCC 3		6·2	7·8405	7·8395
CC 3		9·4	7·8384	
DD 0	1·350	0	7·8288	7·8284
DDD 0		0	7·8279	
DD 4		1·6	7·8305	7·8288
DDD 4		2·3	7·8271	

SOLUBILITY IN ACID.

As already mentioned, determinations of potential differences between strained and unstrained iron indicate a tendency for the former to dissolve more rapidly in acid media than the latter. Heyn and Bauer [1] found this to be true in the case of a very mild steel (0·07 per cent. carbon), a rough proportionality existing between the elongation and solubility. This is confirmed and shown to hold for steels containing up to 1·35 per cent. of carbon

[1] Heyn and Bauer, *Journal of the Iron and Steel Institute*, 1909, No. I. p. 109.

by the following results, which were obtained by immersing the test-pieces in 25 litres of 0·1 per cent. sulphuric acid contained in a large glass tank. The acid was twice renewed, and the experiment lasted eight days.

TABLE III.—*Results of Acid Tests.*

Sulphuric acid—0·1 per cent. Duration—8 days.

Test-Piece.	Carbon per Cent.	Elongation per Cent.	Loss in Weight. Grammes.	Loss per Square Inch.	Relative Corrosion.
AAA 0	0·174	0	0·404	0·222	100
2		17·2	0·516	0·285	128
3		42·2	0·977	0·553	249
BBB 0	0·467	0	1·290	0·674	304
2		12·5	1·587	0·844	380
1		17·2	2·135	1·134	511
CCC 0	0·920	0	2·437	1·306	589
3		6·2	2·731	1·487	670
DDD 0	1·350	0	1·407	0·756	340
4		2·3	1·634	0·918	414

These results are shown graphically in Fig. 2. In every case the rate of solution is greatly enhanced by the strain. Inci-

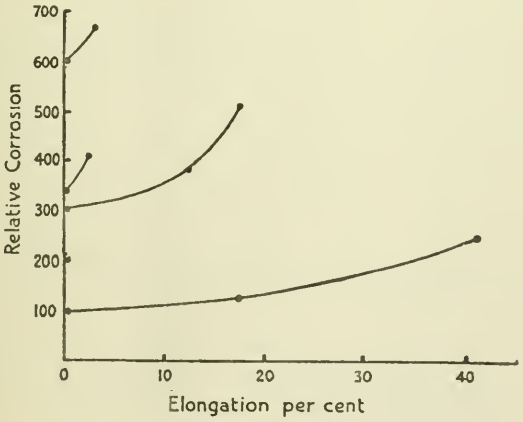


FIG. 2.

dentally it is interesting to note the maximum solubility of the steel near the eutectic point (0·9 per cent. carbon). This is in entire harmony with earlier investigations.

Corrosion in Neutral Solution.

Upon this branch of the subject no reliable data appear to have been published, and electrochemical data have already been shown to be untrustworthy. Experiments have been carried out as follow:

1. Two series of continuous tap water immersion tests of 4 and 6½ months' duration respectively.
2. One series of continuous immersion tests in artificial sea-water for 4 months.
3. One series of alternate wet and dry exposures for 6 months.

The results are given in Tables IV. and V. The data under *relative corrosion* are in every case calculated relatively to the unstrained bar of similar chemical composition, the loss in weight of which is taken as 100. The specimens exhibit a remarkably close agreement, there being no perceptible difference in corrodibilities between the strained and unstrained metals in neutral media.

This highly interesting result must not be taken to mean that a strained steel structure is no more likely to corrode than one that is unstrained. It must be remembered that the specimens used in this research were not only uniformly strained throughout—a condition unlikely to occur in practice—but they were galvanically isolated during the tests by resting on blocks of paraffin wax, so that electrical contact was impossible. Now in practice if a metal is strained at any point, it is the area of contact between the strained and unstrained (or less strained) portions that suffers severely, one part acting anodically to the other during part or the whole of the exposure. It will be clear that in these circumstances even reversal of polarity will not reduce the sum total of corrosion; indeed it may accelerate corrosion by drawing it to fresh areas which were at first cathodic and more or less immune. These results are in perfect harmony with the colloid theory of corrosion.

TABLE IV.—*Corrosion of Strained Steels in Neutral Media.*

Test-Piece.	Carbon per Cent.	Elongation per Cent.	Alternate Wet and Dry (6 Months).			Continuous Tap-water Immersion (4 Months).		
			Loss in Weight. Grammes.	Loss per Square Inch.	Relative Corrosion.	Loss in Weight. Grammes.	Loss per Square Inch.	Relative Corrosion.
A 0	0·174	0·0	0·789	0·308	100	0·274	0·107	100
2		10·9	0·824	0·323	105	0·292	0·114	107
1		14·1	0·800	0·318	103	0·283	0·112	105
3		18·7	0·739	0·294	95	0·296	0·118	110
B 0	0·467	0·0	0·725	0·297	100	0·298	0·122	100
2		9·4	0·715	0·298	100	0·293	0·122	100
3		12·5	0·749	0·309	104	0·306	0·126	103
C 0	0·920	0.0	0·828	0·322	100	0·323	0·126	100
1		3·1	0·745	0·308	96	0·308	0·127	101
3		4·7	0·838	0·333	103	0·326	0·129	102
4		10·9	0·764	0·307	96	0·321	0·129	102
D 0	1·350	0·0	0·857	0·353	100	0·307	0·126	100
3		3·1	0·867	0·364	103	0·320	0·134	106

TABLE V.—*Corrosion of Strained Steels in Neutral Media.*

Test-Piece.	Carbon per Cent.	Elongation per Cent.	Continuous Tap-water Immersion (6½ Months).			Artificial Sea-water Immersion (8 Months).		
			Loss in Weight. Grammes.	Loss per Square Inch.	Relative Corrosion.	Loss in Weight. Grammes.	Loss per Square Inch.	Relative Corrosion.
AA 0	0·174	0·0	0·330	0·174	100	0·438	0·231	100
2		17·2	0·326	0·177	102	0·431	0·233	101
3		34·4	0·320	0·170	98	0·436	0·232	100
BB 0	0·467	0·0	0·350	0·181	100	0·473	0·245	100
2		9·4	0·355	0·181	100	0·478	0·243	99
3		10·9	0·335	0·181	100	0·467	0·253	103
4		29·7	0·361	0·180	100	0·493	0·245	100
CC 0	0·920	0·0	0·388	0·190	100	0·521	0·256	100
3		9·4	0·346	0·183	97	0·486	0·256	100
DD 0	0·351	0·0	0·374	0·180	100	0·462	0·223	100
4		1·6	0·385	0·186	103	0·468	0·226	101

Influence of Carbon.

Attention has already been directed to the enhanced solubility of the steels in dilute acid with increasing carbon content, until the eutectic point is reached, after which the solubility falls. It is interesting to compare the behaviour of the steels in neutral media, and to facilitate this the data for the unstrained specimens are summarised in Table VI.

Table VI.—*Relative Corrodibilities of Unstrained Steels in Neutral Media.*

Steel.	Carbon per Cent.	Loss in Weight (Grammes).				Relative Corrosion.
		Tap-water (4 Months).	Tap-water (6½ Months).	Alternate Wet and Dry (6 Months).	Sea-water (8 Months).	
A	0·174	0·308	0·174	0·107	0·231	100
B	0·467	0·297	0·181	0·122	0·245	103
C	0·920	0·322	0·190	0·126	0·256	109
D	1·350	0·353	0·180	0·126	0·223	108

It will be seen that there is a decided tendency for the corrodibility to rise to the eutectic point, where there is, in most cases, a break in the curve. These results are in entire harmony with those of earlier investigations.[1]

[1] See Chappell, *Chemical News*, 1911, vol. civ. p. 155; *Journal of the Iron and Steel Institute*, 1912, No. I. p. 270; Aitchison, *Transactions of the Faraday Society*, 1916, vol. xi. p. 212; Hadfield and Friend, *Journal of the Iron and Steel Institute*, 1916, No. I. p. 48.

PART IV.

INFLUENCE OF TEMPERATURE UPON THE RATE OF CORROSION OF IRON IMMERSED IN WATER.

As is well known, the majority of chemical reactions are accelerated by rise of temperature, and the corrosion of iron is no exception to the rule. The problem, however, is complicated by the fact that the solubility of oxygen falls with rise of temperature, becoming nil at the boiling point, under which conditions iron does not corrode. It is to be anticipated, therefore, that the rate of corrosion will rise with the temperature to a maximum, and then fall as the rate of oxidation exceeds that at which the dissolved oxygen can diffuse towards the metal.

But little quantitative work, however, has been carried out on the subject, probably owing to the extreme difficulty of obtaining reliable "repeat" results. The earliest work was that of Mallet,[1] who states that the maximum corrosion takes place at 79° to 88° C. in the case of iron immersed in shallow trays of water. No actual numerical data are given.

Heyn and Bauer,[2] on the other hand, suspended mild steel plates in glass vessels fitted with reflux condensers to prevent loss by evaporation. Their results were as follow:

Temperature, °C.	20	40	60	80	90	100
Relative corrosion	100	257	357	311	305	105

The duration of the experiments was twenty-two days. The maximum corrosion took place at 60° C. The results, however, are of doubtful value, because the precautions adopted to prevent evaporation likewise prevented proper access of air.

The present research was therefore undertaken with a view to throwing further light on this difficult problem.

[1] Mallet, *British Association Reports*, 1840, p. 229.

[2] Heyn and Bauer, *Mitteilungen aus dem Königlichen Materialprüfungsamt*, Berlin, 1910, vol. xxviii. p. 104.

Sources of Error to be Avoided.

The extreme difficulty of obtaining satisfactory "repeat" results is well known to all investigators of ferrous corrosion, and before the main portion of this research could be undertaken it was necessary to investigate and attempt to eliminate all possible influences.

1. *Selection of the Metal.*—It is very difficult to obtain series of iron plates perfectly homogeneous in character, and sufficiently similar in their physical condition and chemical composition to corrode at precisely the same rate under identical conditions.

Many cases of erratic corrosion are due entirely to superficial chemical or physical variation, and it not infrequently happens that, whilst two or more plates when subjected for the first time to corrosive influences exhibit marked differences in their rates of corrosion, when they are cleaned and for a second time are exposed exhibit very fair uniformity.

Thus, three pieces each 1 decimetre square were cut from a sheet of open-hearth steel, No. 30, B.W.G. The scale was removed by immersion in dilute acid; the plates were then thoroughly washed, rinsed with dilute alkali to remove any trace of acid within the pores, again washed, dried, and polished with emery. They were then suspended for three weeks in a large tank of water at a mean temperature of 14° C. They were then removed, rubbed clean, and weighed, the losses in weight being as follow:

(1) 0·490 (2) 0·500 (3) 0·442 (grammes).

The extremes manifest a difference of 12 per cent. The same plates were again polished and immersed for a second period of three weeks, the mean temperature being 19·6° C. The losses were:

(1) 0·522 (2) 0·531 (3) 0·541

Plates (1) and (2) manifest the same percentage difference as before, but plate (3) has now fallen into line, the extreme differences, namely between (1) and (3), being less than 4 per cent.—an agreement which, for commercial material, may be regarded as very satisfactory.

In order to reduce such possible variation to a minimum it

was decided to employ thin sheets of Kahlbaum's pure electrolytic iron foil from a small pre-war stock possessed by the author, ten pieces being chosen after their suitability had been ascertained by a series of preliminary trials. These sheets were used repeatedly and gave fairly consistent results. Experience soon showed that in this type of work results agreeing within 3 per cent. must be regarded as quite satisfactory, whilst if within 1 per cent. the agreement is extraordinarily close. For even metal of this purity does not always give uniform results. Thus three pieces were exposed to subaqueous corrosion for five days at 12° C. and the following relative losses in weight noted:

(1) 100 (2) 92 (3) 101

Here plate (2) is eccentric. Upon a second exposure, this time at 22° C., the same plates lost relatively as follows:

(1) 100 (2) 105 (3) 122

plate (3) exhibiting marked irregularity. A third exposure yielded

(1) 100 (2) 95 (3) 95

In this case plate (1) is irregular.

The only possible explanation for these eccentricities appears to lie in some internal irregularity which becomes superficial as successive layers of metal are removed as rust.

By carrying out a large number of tests, and plotting all the results on a corrosion-temperature diagram, as shown in Figs. 1 and 3, a mean curve of fair relative accuracy can be drawn, however. The number of experiments that can be carried out simultaneously is severely limited by the supply of material and causes the research to be unduly protracted. Consequently several other factors have to be taken into consideration, which would cancel out normally if all the experiments could be conducted at the same time.

2. *Oxygen Pressure.*—The rate of corrosion of iron is directly proportional to the amount of dissolved oxygen, and hence to the partial pressure of oxygen in the atmosphere. This was experimentally demonstrated by Walker and his co-workers.[1] In order, therefore, to render the results obtained on different occasions strictly comparable, it is necessary to make a correction

[1] Walker, Cederholm, and Bent, *Journal of the American Chemical Society*, 1907, vol. xxix. p. 1251.

for the variation in oxygen pressure in the atmosphere. This is most conveniently done by assuming it to be directly proportional to the mean barometric height during the period of the experiment. Although not strictly accurate, it is sufficiently close for the purpose.

3. *Depth of Immersion.*—The rate of corrosion falls with increasing depth of immersion. It is essential, therefore, to maintain a constant water-level in the corrosion vessels. This is a problem of considerable difficulty at temperatures appreciably above atmospheric, and the methods adopted are described in the sequel.

4. *Duration of Experiment.*—The assumption is made throughout this research that where the difference in the durations of any two or more experiments is small, the rate of corrosion is directly proportional to the length of exposure. Owing to the difficulty of controlling the experiments at and below room temperatures over week-ends, the tests in Method II. were run from Mondays till Saturdays inclusive, that is approximately 120 hours. Extreme difficulty was experienced in obtaining data at temperatures slightly below those of the laboratory. They were effected by causing tap water to circulate through regulated thermostats, and carrying out the experiments at different periods of the year. Sudden frosts could be guarded against with thermo-regulators which fixed the lowest temperature to which it was desired the bath should fall. Sudden rises in temperature, however, could not be controlled, and if these took place in the middle of the week, the experiments were spoiled.

5. *Illumination.*—Exposure to diffused daylight tends to accelerate corrosion. This was quantitatively demonstrated by Cribb and Arnaud [1] in 1905, and has been confirmed by other investigators.[2] In criticising the experiments of the present author Professor Armstrong [3] suggested that the effect was due to differences in temperature rather than to the light itself. Experiments have therefore been carried out in which it is believed all irregularities due to temperature differences have been removed.

[1] Cribb and Arnaud, *Analyst*, 1905, vol. xxx. p. 225.

[2] Friend, *Carnegie Scholarship Memoirs*, 1911, vol. iii. p. 1; Friend, West, and Bentley, *Journal of the Iron and Steel Institute*, 1912, No. I. p. 259.

[3] Armstrong, *ibid.*, 1912, No. I. p. 269.

Four plates of electrolytic iron foil, measuring 7 × 6 square centimetres and weighing approximately 5 grammes, were placed, one each, in cylindrical jars of similar shape, two of glass and two of glazed earthenware. These were immersed in a large rectangular glass tank, of about 40 litres capacity, filled with tap water, and placed near a window.

Although the plates in the earthenware jars were not absolutely in the dark, they were fairly well shaded. It was difficult to arrange for them to be in entire darkness, and at the same time to provide a free air circulation, and a temperature exactly similar to that to which the illumined plates were exposed. The temperatures were taken at frequent intervals, but in no case was a difference so great as 0·1° C. observed between any of the four specimens.

After ten weeks the plates were rubbed clean, dried, and weighed, with the following results :

TABLE I.

Condition.	Loss in Weight. Grammes.	Mean Loss in Weight. Grammes.	Relative Losses in Weight.
Light . . .	0·4746 0·4775	0·4761	100·0
Dark . . .	0·4112 0·3942	0·4027	84·6

It is evident that light stimulates the corrosion of iron *per se*, and quite apart from any temperature effect which, if not controlled, would still further enhance corrosion. As these experiments were carried out during February, March, and April, it is evident that the actual influence of diffused sunlight is appreciably greater than is indicated above, for during the long winter nights all the plates would be corroding in the dark and thus at the same rate.

As it is impossible to render the intensity of the daylight perfectly uniform in different series of protracted experiments carried out at different periods of the year, it is evident that for strictly comparative purposes the tests should be carried out in the dark. This is difficult to arrange at the same time ensuring

free circulation of fresh air. The specimens in this research were therefore shielded from direct sunlight, and as far as possible the periods of exposure were regulated to contain a fairly constant proportion of daylight hours. In the second method of experiment described below, glazed earthenware jars were employed throughout, so that the plates were well shaded even when the laboratory was well illuminated.

6. *Cleaning.*—Rust does not usually adhere to the metal very tenaciously under the conditions of the experiments now under consideration, if after removal from the corroding vessels it is not allowed to become dry. The plates were washed, rubbed with a cloth, and dried by gently warming in a Bunsen flame, all these operations being carried out immediately after removal from the water. In this way only was it found possible to obtain consistent results. In the neighbourhood of 0° C. the loss in weight in five days was only about 0·03 gramme, so that any small error due to imperfect cleansing caused disproportionately large errors in the results, a difference of 1 milligramme affecting them by more than 3 per cent.

7. There still remains one factor, however, for which it has not been found possible to apply a correction. Adeney and Becker have shown[1] that the rate at which air dissolves in water is enormously influenced by its state of humidity, quite apart from any question of reduced partial pressure due to the presence of water vapour. Dry air is much more rapidly absorbed than moist, and variation in atmospheric humidity must in consequence very appreciably affect the rate of corrosion of submerged iron. This serves to explain some of the divergences amongst the data given below. Probably, however, the mean values for the different sets of results as given in Table IV. are fairly trustworthy.

Method I.

An attempt was made to repeat Mallet's experiments by determining the rate of corrosion of iron in shallow dishes. Plates of polished iron foil were laid flat in glass crystallising dishes, covered to a depth of 3·3 centimetres with distilled water, and floated in thermostats. Each plate weighed about 8 grammes and

[1] Adeney and Becker, *Scientific Proceedings of the Royal Dublin Society*, 1920, vol. xvi. p. 143.

measured approximately 7·5 centimetres square. The results are given in Table II., and shown graphically in Fig. 1, in which the black points represent the individual data and the circles the mean results as given in column 7 of the table.

TABLE II.

1. Temp. °C.	2. Time. Hours.	3. Mean Height of Barometer. Cms.	4. Loss in Weight. Grammes.	5. Loss in Milligrams per Square Decimetre per Hour at 76 cms.	6. Mean Temp. ° C.	7. Mean Loss.	8. Relative Corrosion.
			Calculated		0	0·700	1·00
1·20	79·75	75·0	0·0250	0·587			
2·13	39	74·2	0·0129	0·628			
2·63	39	74·2	0·0164	0·797	2·30	0·722	1·03
2·75	39	74·2	0·0160	0·784			
2·78	39	74·2	0·0167	0·816			
4·3	36·3	74·3	0·0142	0·742	4·45	0·752	1·07
4·6	36·3	74·3	0·0146	0·762			
10·0	56	74·5	0·0156	0·527			
10·8	79·75	75·0	0·0311	0·730	11·28	0·766	1·09
11·6	93	75·2	0·0410	0·794			
12·7	69·5	74·1	0·0370	1·011			
15·2	41	75·7	0·0207	0·961	15·25	0·950	1·36
15·3	41	75·7	0·0212	0·939			
20·5	56	74·5	0·0408	1·376	20·5	1·376	1·97
26·4	69·5	74·1	0·0633	1·730			
26·6	93	75·2	0·1083	2·148			
26·6	79·75	75·0	0·0829	1·944	26·63	1·958	2·80
26·7	56	74·5	0·0659	2·223			
26·7	41	75·7	0·0379	1·719			
26·8	41	75·7	0·0438	1·986			
36·4	47	74·6	0·0567	2·276	36·55	2·314	3·31
36·7	47	74·6	0·0586	2·352			

Loss by evaporation only became serious at temperatures above 20° C., and was compensated by frequent small additions of distilled water. This introduced considerable temperature fluctuation, and the variation in the individual results appears to be largely attributable to this cause. The method was clearly

unsuited for higher temperatures and was therefore discarded in favour of Method II., described below. The mean results for the temperatures investigated, however, agree quite well with

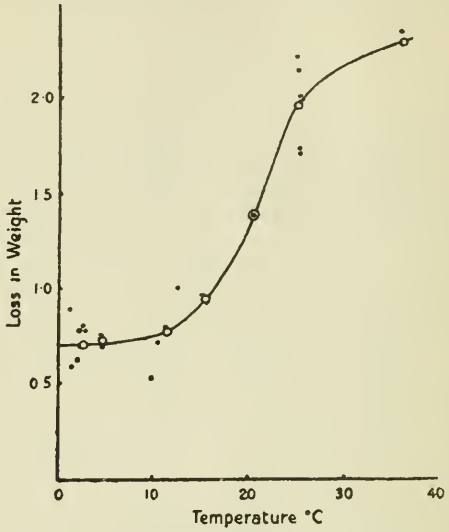


Fig. 1.

those found by Method II., a curve on the corrosion-temperature diagram being obtained which is hyperbolic in form. The bend in the curve at 26° C. is referred to in the sequel.

Method II.

The arrangement is shown in Fig. 2. Sheets of foil approximately 7·2 centimetres square were suspended by glass hooks in glazed earthenware jars of water maintained at constant temperatures in thermostats. The water in the latter was preserved from undue evaporation at temperatures above 50° C. by a layer of molten paraffin wax. Evaporation in the corrosion jars was counterbalanced by syphons connected with a large reservoir of distilled water maintained at constant level. By this arrangement satisfactory results could be obtained up to about 70° C. Above this, owing to the rapid rate of evaporation and the clogging of

the tubes with released air, difficulties were encountered in maintaining a constant temperature and level over night. Further, it was found that the results were being affected by the continuous circulation of fresh, oxygenated water from the reservoir. The syphon was therefore disconnected, and the water in the jars covered with a thin layer of molten paraffin wax, which had been carefully purified by boiling with distilled water. This did not entirely prevent evaporation but reduced it to such a small amount that it was only necessary to compensate by the addition of a few drops of water occasionally. As a result the temperature

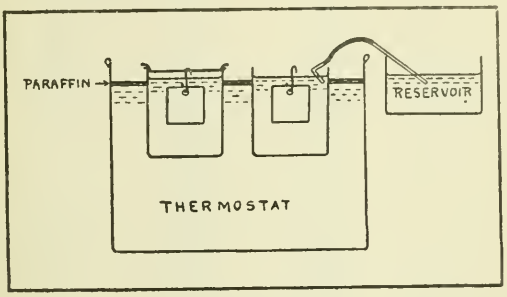


Fig. 2.

closely approximated to that of the bath and remained very uniform throughout.

These results under wax were, however, constantly spoiled by the oxide forming a closely adhering coat which tended to preserve the underlying metal, and which was also exceedingly difficult to remove. It is doubtful, therefore, if these data, despite the uniformity of the other conditions, possess greater reliability than those obtained without wax.

The results are given in Table III. and shown graphically in Fig. 3. The data obtained when the water in the jars was waxed, marked W in the table, are slightly lower in consequence of the resulting retardation in the rate of diffusion of the oxygen to the water below. They are indicated by the lower curve connecting the small circles. Assuming the retardation to be a constant amount, the corrosion curve in free water should follow a parallel course, and the portion extrapolated on this assumption is represented by the broken line to the right of 80° C.

Table III.

Temp. °C.	Duration. Hours.	Mean Height of Barometer. Centimetres.	Loss in Weight. Grammes.	Loss in Milligrammes per Square Decimetre per Hour at 76 cms.	Relative Corrosion.
0		Calculated		0·420	1·000
1·5	111	74·89	0·0477	0·436	1·04
1·5	111	74·89	0·0500	0·457	1·09
2·1	99	75·69	0·0413	0·420	1·00
2·4	99	75·69	0·0403	0·410	0·98
2·4	99	75·69	0·0433	0·440	1·05
3·0	99	75·12	0·0368	0·376	0·90
10·0	115	76·00	0·0662	0·614	1·46
10·5	120	75·51	0·0519	0·435	1·04
10·5	120	75·51	0·0546	0·458	1·09
11·6	119	75·20	0·0604	0·513	1·22
11·6	119	75·20	0·0654	0·556	1·33
11·6	119	75·20	0·0659	0·560	1·35
13·5	114	76·22	0·0611	0·534	1·28
15·3	112	75·32	0·0604	0·512	1·22
15·4	112	75·32	0·0567	0·545	1·30
16·7	112	75·14	0·0619	0·559	1·35
16·7	112	75·14	0·0643	0·580	1·40
18·1	112	75·92	0·0674	0·602	1·44
18·1	112	75·92	0·0702	0·623	1·49
18·3	119	75·64	0·0805	0·681	1·62
19·7	117	75·72	0·0822	0·705	1·68
22·0	80	75·05	0·0746	0·945	2·25
22·2	113	75·51	0·0988	0·880	2·10
22·2	113	75·51	0·1044	0·930	2·22
22·2	113	75·51	0·1208	1·076	2·56
22·3	110	75·73	0·1094	0·998	2·38
25·0	112	75·83	0·1099	0·983	2·34
27·5	112	75·83	0·1082	0·970	2·31
29·3	114	74·89	0·1253	1·115	2·65
29·3	114	74·89	0·1259	1·120	2·67
29·5	114	74·89	0·1323	1·177	2·80
32·6	116	75·27	0·1207	1·051	2·50
36·5	116	75·27	0·1368	1·192	2·84
41·6	111	75·03	0·1510	1·378	3·28
44·1	111	75·03	0·1699	1·550	3·70
53·1	118	75·14	0·2126	1·821	4·34
60·8	97	75·73	0·2302	2·379	5·66
69·5	111	75·72	0·2964	2·680	6·38
70·2	115	76·00	0·2950	2·565	6·11
79·2	111	75·64	0·3322	3·008	7·16
W75·5	115	76·00	0·3092	2·690	...
W83·0	92	74·97	0·2516	2·773	...
W89·7	112	75·51	0·2772	2·491	...
W90·0	112	75·51	0·2853	2·564	...
W96·0	110	74·89	0·2260	2·085	...

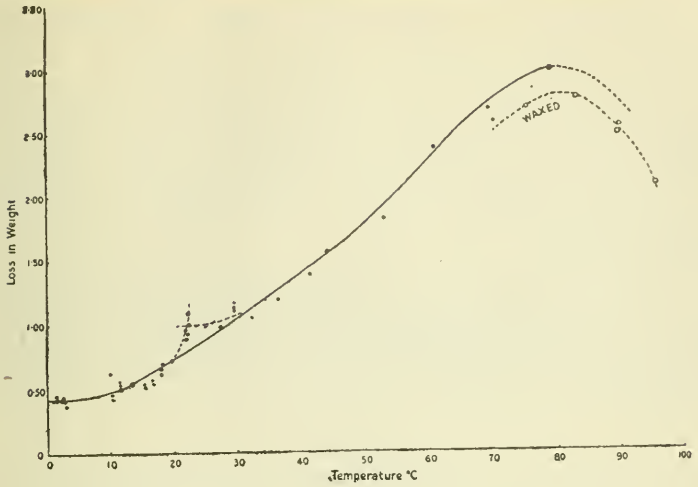


FIG. 3.

Consideration of these results reveals several interesting features.

1. At the lower temperatures the corrosion curve tends to assume hyperbolic form. The rate of corrosion increases to a maximum at about 80° to 85° C., and then rapidly falls.
2. At its temperature of maximum corrosion iron rusts approximately seven times as rapidly as at 0° C., corresponding on an average to 9 per cent. increase on the corrosion at 0° C. per one degree rise in temperature. Actually the increase is greater than this at some temperatures, notably ordinary atmospheric, since in the neighbourhood of 0° C. to 10° C. there is relatively little change.
3. The results seem to indicate a slight bend in the curve at 22° C. The same observation was made with Method I., and three hypotheses suggest themselves.
   a. This may be a peculiarity of the particular iron employed.
   b. It may result through some systematic error in the experiments.
   c. There may be normally a break in the curve at or near this point.

Experiments are in progress with various commercial steels with a view to throwing further light upon this point. It may, however, be mentioned that the third hypothesis is quite in harmony with the author's colloid theory of corrosion (see Part V.). Colloidal iron hydroxide is heavily hydrated, and any change in its degree of hydration with rise of temperature may reasonably be expected to affect the size of its particles and hence its catalytic activity.

Assuming there be no break in the curve at this temperature, and that the rate of corrosion with rise of temperature be represented by the continuous line, the relative corrodibilities at various temperatures are seen to be as follow, when that at 0° C. is taken as unity :

TABLE IV.

Temperature, °C.	Relative Corrosion.	Temperature, °C.	Relative Corrosion.
0	1·00	35	2·90
10	1·13	40	3·31
15	1·40	50	4·24
20	1·74	60	5·44
25	2·10	70	6·58
30	2·50	80	7·20

PART V.

THE COLLOID THEORY OF CORROSION.

Any satisfactory theory of corrosion must be capable of explaining the following fundamental facts :

1. *Iron does not rust in dry air.* The author has many tubes in which pure electrolytic iron foil has been kept for thirteen years in contact with air dried over phosphorus pentoxide, and not one shows the slightest sign of oxidation or tarnish. If, however, the metal is heated in contact with this very dry air, a thin superficial layer of oxide is formed, giving rise to the well-known tempering colours. But this is not rust.

2. *Iron does not rust in pure liquid water* in the entire absence of air. Pure Swedish iron has been kept by the author for twelve years under these conditions and, apart from the merest trace of tarnishing, which could only be detected under a bright light, there was no apparent change. Even at its boiling point water has no action on the compact metal, although the finely divided metal decomposes it with evolution of hydrogen.

3. *Iron does not rust in moist air at constant temperature,* provided no liquid water condenses on its surface. It is when the temperature fluctuates below the dew point that corrosion takes place.[1] In other words, **liquid water is essential to corrosion.** This finally disposes of the idea that corrosion is a simple case of direct oxidation.

Of the various theories advanced to account for the corrosion of iron, two only call for consideration here. Of these the older is the so-called *acid theory* which was summarised by Calvert [2] in 1871, according to which water and air alone cannot induce the corrosion of iron. An acid substance must also be present to enable the iron first to pass into solution. Since in most cases of natural corrosion carbonic acid is one of the chief accelerators

[1] Dunstan and Co-workers, *Transactions of the Chemical Society*, 1905, vol. lxxxvii. p. 1557.

[2] Calvert, *Chemical News*, 1817, vol. xxiii. p. 98.

of the reaction, the changes taking place may be represented by the following equations :

$$\text{(i)}\ Fe + 2CO_2 + 2H_2O = \underset{\text{Soluble ferrous bicarbonate.}}{FeH_2(CO_3)_2} + 2H$$

$$\text{(ii)}\ FeH_2(CO_3)_2 + Aq. = FeO.Aq. + H_2O + 2CO_2$$

$$\text{(iii)}\ 4FeO.Aq. + O_2 = \underset{\text{Rust.}}{2Fe_2O_3\ Aq.}$$

The nascent hydrogen liberated in accordance with equation (i) combines with dissolved oxygen to form water. The carbon dioxide liberated by the hydrolytic decomposition of ferrous bicarbonate, as shown in equation (ii), is free to attack more iron. Thus a small quantity of acid is able to assist catalytically in the oxidation of an indefinite quantity of metal. This theory has frequently been termed the *carbonic acid theory of corrosion*, but such a term is too restricted, for almost any acid is capable of acting in the above manner. Neither is it essential that the acid should be free, for neutral salts, such as sodium chloride, even when rendered faintly alkaline, readily stimulate corrosion. In other words, according to modern views, small quantities of an electrolyte are assumed to be necessary to induce corrosion.

In 1903, Whitney [1] suggested a somewhat different explanation, according to which, water being an electrolyte and therefore split up to a small extent into hydrogen and hydroxyl ions, it is unnecessary to postulate the existence of a catalyst before corrosion can take place.

Thus, the condition of equilibrium between liquid water and its ions may be represented by the scheme :

$$nH_2O \rightleftharpoons (n-1)H_2O + H^{\cdot} + OH'$$

On placing iron in the water, some of the metal passes into solution in the ionic condition, an equivalent amount of hydrogen being liberated on the surface of the undissolved metal. Thus :

$$Fe + 2H^{\cdot} + 2OH' \rightleftharpoons Fe^{\cdot\cdot} + H_2 + 2OH'$$

Admission of oxygen to the system removes the liberated hydrogen by converting it into water, so that increasing quantities of iron pass into solution until saturation is reached, when hydrated

[1] Whitney, *Journal of the American Chemical Society*, 1903, vol. xxv. p. 394.

ferrous oxide, more or less oxidised by excess of air to the ferric condition, precipitates out.

According to this theory, therefore, pure liquid water and oxygen are alone sufficient to cause the formation of rust.

At first sight it would appear very easy to decide between the two theories, but in practice it is found to be extremely difficult, owing to the elaborate precautions that must be taken to ensure the purity of the materials.

The former theory has received strong support from the researches of Moody [1] and others,[2] and also is in perfect accord with the well-known fact that, as the methods of preparing pure substances become increasingly refined, the number of reactions known to occur between impure reagents but not between them when exceedingly pure, steadily grows.

Whitney's theory is frequently termed the "electrolytic" theory of corrosion. This is distinctly misleading and has led to much confusion because, by implication, the former theory is not to be regarded as electrolytic. In point of fact, both theories will bear equally well the electrolytic interpretation.

The difference, however, is mainly one of academic rather than of technical interest, since absolutely pure air, water, and metal are practically unobtainable. Consequently iron invariably rusts in contact with air and liquid water.

For many years the author has realised that neither of the above theories is sufficient to account for all the phenomena connected with the corrosion of iron.

In 1910 Heyn and Bauer [3] called attention to the fact that if iron is allowed to corrode in moving water, the rate of corrosion at first rises rapidly with the rate of flow. A maximum is soon reached, however, after which further increase in the rate of flow causes the corrosion to decline. The method of experiment consisted in suspending sets of two mild steel plates in beakers, each of 600 cubic centimetres capacity, and through which uniform streams of water were continuously maintained for a period of three weeks, from glass delivery tubes connected with the water supply of the laboratory. The rates of flow of the

[1] Moody, *Transactions of the Chemical Society*, 1906, vol. lxxxix. p. 720.
[2] Friend, "The Corrosion of Iron and Steel." (Longmans, 1911.)
[3] Heyn and Bauer, *Mitteilungen Königlichen Materialprüfungsamt*, Berlin, 1910, vol. xxviii. p. 62.

water were expressed as litres per hour, but from the dimensions of the apparatus it is possible to calculate the approximate rates of flow of the water over the surfaces of the plates. The results are as follow :

Velocity of water—				
(i) Litres per hour . .	0	15	50	350
(ii) Feet per hour . .	0	11	36	250
Relative corrosion [1] . .	100	240	146	67

Experiments carried out with cast-iron plates yielded analogous results.[2] The method, however, does not admit of the attain-

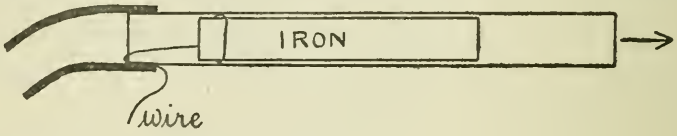


Fig. 1.

ment of very high velocities, the maximum reached by Heyn and Bauer being only 250 feet per hour.

In order to determine whether or not it might be possible to inhibit the corrosion of iron altogether at higher speeds, strips of Kahlbaum's electrolytic iron foil were held in wide glass tubes by means of platinum wire, and connected directly to the water-mains, as shown in Fig. 1.

By this method the water could be made to flow over the surface of the metal at any velocity up to about six miles per hour. The results were as follow :

Table I.

Velocity of Water.		Loss in Weight of Iron. Milligrammes per Hour.	Relative Corrosion.	Remarks.
Feet/Hour.	Miles per Hour.			
0	0	0·082	100	Rust.
540	0·1	0·188	229	,,
570	0·1	0·177	216	,,
4,200	0·8	0·054	66	,,
9,000	1·8	0·029	35	Traces of rust
13,000	2·3	0·032	39	,,
30,000	5·8	0·045	55	No corrosion

[1] Means of two results each.

[2] See p. 62.

These results are shown graphically in Fig. 2. On increasing the rate of flow of the water, corrosion at first increases, then falls to a minimum at a velocity of about two miles per hour, and finally very slowly increases. This latter increase is probably due to mechanical erosion, for no trace of rust is visible.

In order to be sure that lack of aeration of the water was not the cause of the reduced corrosion, the experiments were varied by introducing a side tube between the metal and the main water supply, into which air was sucked as the water flowed

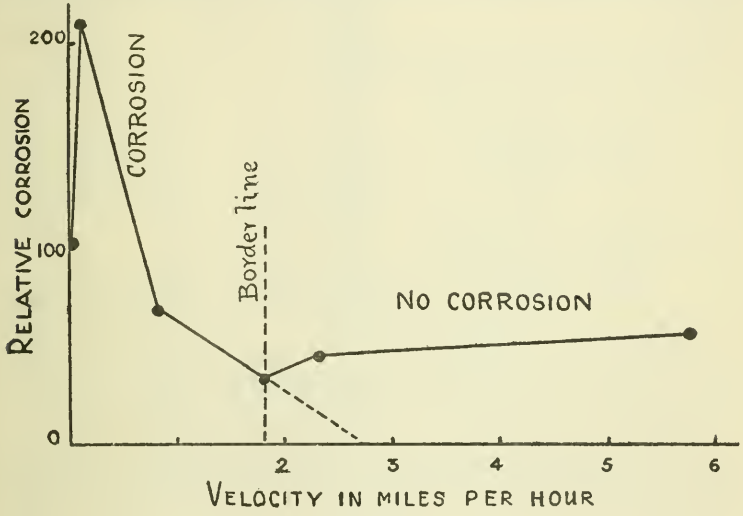


FIG. 2.

through the tube. The surface of the metal was then swept by water, rendered milky with minute bubbles of air. The results, however, were substantially the same.

In order to confirm these remarkable observations, the author requested his friend, Dr. Hatfield, to repeat the experiments with Sheffield water. This was particularly desirable in view of the fact that the experiments described above were carried out with Worcester City tap water, which is known to contain an abnormal quantity of dissolved salts on account of the proximity of the Severn to the Droitwich salt springs. The experiments could not be repeated with distilled water on account of the immense volume required.

Dr. Hatfield's report was as follows :

" The samples of foil were polished to 000 emery-paper and suspended by platinum wire in a glass tube of suitable diameter, as suggested. The period of test was forty-eight hours in each case. The temperature of the water was constant at 8° C. during the whole test.

" In the test with water at high velocity the rate of flow varied with a minimum of 2·02 miles per hour (during the day) to a maximum of 5·17 miles per hour (during the night). In the test with water at low velocity the rate of flow varied from $\frac{1}{10}$ to $\frac{1}{8}$ mile per hour."

The following data were obtained :

i. Water at high velocity—
No rust formed.
Loss in weight—14 milligrammes per square decimetre.

ii. Water at low velocity—
Definite rusting.
Loss in weight—109 milligrammes per square decimetre.

These results entirely confirm those of the present author. It was thought desirable next to determine whether or not the same retardation is manifested in acid solution.

Experiments to this end were undertaken by Mr. J. H. Dennett, B.Sc., in conjunction with the author. The method consisted [1] in attaching a disc of pure iron foil to a bronze axle, contact between the two metals being prevented by rubber washers. The axle was made to rotate at varying speeds, its lower end, carrying the iron disc, being immersed in a glass tank containing a litre of dilute sulphuric acid. The internal walls of the tank possessed raised vertical ribs, which greatly reduced the tendency of the liquid to swirl round with the rotating disc. The amount of iron dissolved was determined by titration with permanganate. The same disc of iron was used throughout the research in order to avoid fluctuations due to chemical and physical variations characteristic of different samples of the metal. The driving power was obtained from a $\frac{1}{4}$ horse-power electric motor, a maxi-

[1] See Friend and Dennett, *Transactions of the Chemical Society*, 1922, vol. cxxi. p. 41.

mum velocity of 4000 revolutions per minute being reached. The arrangement is shown in Fig. 3, and the results, which are

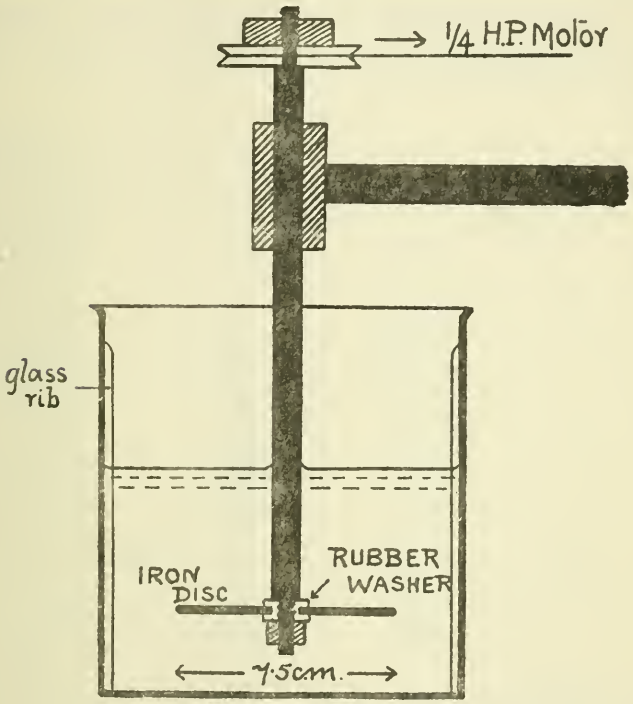


Fig. 3.

given in Table II., are shown graphically in Fig. 4 for the 0·5 per cent. acid.

It will be observed that:

1. The different concentrations of acid yield almost identical results at the same velocities.
2. The rate of solution is directly proportional—within the error of experiment—to the velocity of rotation. Even at 4000 revolutions, corresponding with a rim velocity of thirty-five miles per hour, there is no sign of falling off in the rate of solution. Evidently, therefore, solution of iron in acid is a different process from the corrosion of iron in aerated water. In the latter case, corrosion

ceases at a velocity of three to five miles per hour, as has been seen.

As no other recognised theory of corrosion could account for this remarkable difference in the behaviour of iron towards

TABLE II.

Conc. of H_2SO_4. Per Cent.	Temperature.	Revolutions per Minute.	Relative Rates of Solution.
1·0	12·2	2400	10·24
	13·6	3200	12·38
0·5	10·2	0	**1·00**
	10·0	145	2·11
	9·4	238	2·46
	14·0	300	3·17
	9·8	800	3·32
	13·8	1700	7·62
	12·2	2270	9·18
	12·2	2400	10·24
	12·2	2400	10·00
	13·1	3200	12·24
	14·9	4000	16·90
0·1	9·6	238	2·13
	9·4	238	2·10
	14·0	800	2·95
	13·8	1700	7·47
	12·2	2400	10·00
0·05	13·2	800	3·06
	13·8	1700	7·13

neutral and acid media when in motion, it was evident that a new theory was required. The author was therefore led to suggest the following : [1]

(i) On coming into contact with air and liquid water iron is slowly oxidised to ferrous hydroxide. This compound, however, is produced in the colloidal or sol condition—a state in which it is usual for many substances to be fairly reactive chemically.

(ii) The colloidal ferrous hydroxide oxidises in excess of air to a higher hydroxide, still in colloidal form. In the most favourable circumstances this higher oxide will

[1] Friend, *Transactions of the Chemical Society*, 1921, vol. cxix. p. 932.

be ferric hydroxide ; in less favourable circumstances, more or less colloidal ferrosoferric hydroxide, Fe_3O_4.Aq., will be formed.

(iii) This higher colloidal hydroxide now acts catalytically, accelerating the oxidation of the iron, and simultaneously undergoing reduction to a lower colloidal hydroxide,

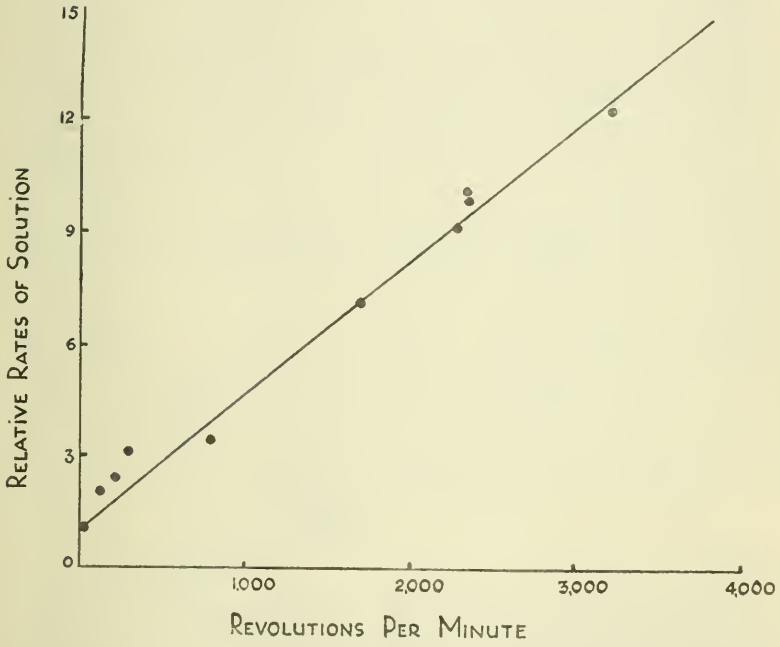


Fig. 4.

only to be oxidised again as oxygen from the air diffuses towards it.

(iv) When the sol (*i.e.* colloid) flocculates or precipitates out, rust is produced.

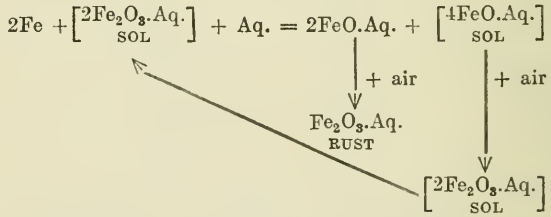
In ordinary cases, therefore, corrosion may be proceeding in two ways at the same time, namely :

1. By a process of solution, rendered possible by the presence of dissolved salts, &c.

2. By catalysis, the catalyst consisting of a colloidal iron hydroxide.

In acid solution, the former of these processes takes place, probably exclusively, for Spring[1] has shown that iron salts in neutral solution invariably give the Tyndall effect, indicating that a sol is present; yet on addition of an acid the effect disappears, suggesting that the sol has passed into solution. In neutral solution, therefore, process 2 predominates, and the rate of corrosion depends almost entirely upon sol formation. Now if the catalysing sol is removed from contact with the iron as rapidly as it is formed, as, for example, with a rapid stream of water, corrosion must be retarded. This explains the phenomenon referred to on p. 129. On the other hand, rapid movement in acid media will facilitate solution by increasing the number of ions that strike the metallic surface in each unit of time.

The foregoing theory may be schematically represented as follows:



It will be evident that a ready method of testing this theory lies in determining whether or not the phenomena of corrosion are influenced by such factors as affect the formation, stability, and precipitation, not merely of sols in general, but of electropositive sols, since iron hydroxide sols are positive. Such sols may be removed or destroyed by other than purely mechanical means, and if the above theory is correct it follows that all processes, whether chemical or physical, which effect the precipitation or destruction of positive colloids should tend to retard corrosion. On the other hand, those which tend to stabilise positive colloids should enhance corrosion. This is found to be the case.

[1] Spring, *Bull. Acad. Roy. Belg.*, 1899, (iii.) vol. xxxvii. p. 174.

Influence of Dissolved Salts upon Corrosion.

As a general rule, if a small quantity of an inorganic salt is dissolved in water in which iron is corroding, the rate of corrosion is enhanced. The rate increases with the salt concentration until a maximum is reached, termed the *critical concentration*.[1] Further concentration of the salt reduces the corrosion, which may ultimately fall to nil, at what is termed the *limiting concentration*.[1] In the majority of cases the solution becomes saturated with the salt long before the limiting concentration is reached. This latter therefore becomes a hypothetical number, as, for example, in the case of the chlorides and sulphates referred to in Fig. 7.

The fall in corrosion in the case of saturated solutions of sodium chloride (brine) was explained by Adie [2] as being the direct result of the reduced solubility of oxygen in the solution, for, as has since been shown,[3] the rate of corrosion is directly proportional to the concentration of dissolved oxygen. Now whilst this is undoubtedly an important factor, it cannot be the only one, in as much as experiment shows that the reduction in corrosion is usually very much greater than the above theory demands. Such was found to be the case, for example, with potassium sulphate solutions at 15° C., as is evident from the following data :

Concentration of K_2SO_4 (grammes per litre)	0	5	10	15	50	100
Relative corrosion [4] . . .	100	70	115	120	23	14
Relative oxygen solubility [5] .	100	97	94	91	80	65

These results are shown in Fig. 5, and it will be evident that if Adie's explanations were complete, the corrosion curve should show a general similarity to the oxygen solubility curve. This is clearly not the case, for whilst the corrosion in the 100 gramme solution has fallen from 100 to 14, the oxygen solubility has only fallen to 65.

[1] Heyn and Bauer, *loc. cit.*, 1908, vol. xxvi. p. 1.

[2] Adie, *Minutes of the Proceedings of the Institution of Civil Engineers*, 1845, vol. iv. p. 323.

[3] Walker and Co-workers, *Journal of the American Chemical Society*, 1907, vol. xxix. p. 1251.

[4] Friend and Barnet, *Journal of the Iron and Steel Institute*, 1915, No. I. p. 336.

[5] Calculated from the data given by MacArthur, *Journal of Physical Chemistry*, 1916, vol. xx. p. 495.

On the other hand, experiments with sodium chloride solutions [1] at 23·5° C. yielded results agreeing quite well with Adie's theory. Thus:

Grammes NaCl per litre	0	5	10	15	30	60	120
Relative corrosion .	100	91	94	95	81	76	60
Relative oxygen solubility	100	97	94	91	84	74	50

A glance at Fig. 6 suffices to show the close similarity between the corrosion and solubility curves.

These apparent anomalies, entirely inexplicable on any of

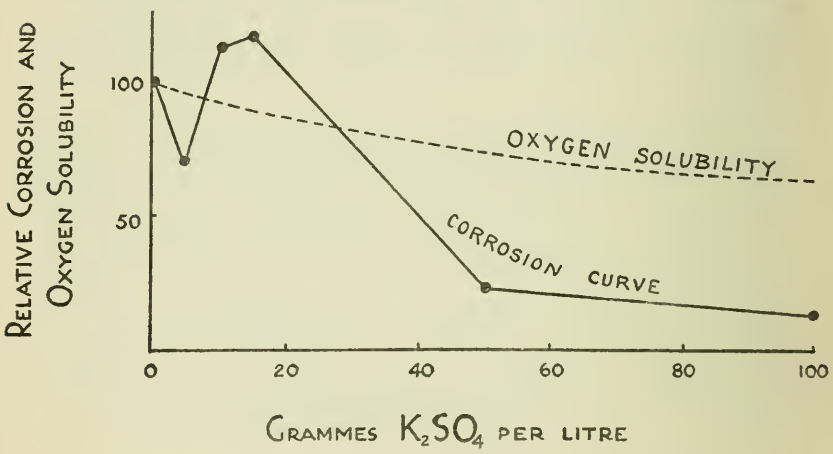


Fig. 5.

the earlier theories of corrosion, are rendered intelligible by the colloid theory.

For many years it has been known that acid radicles, which are electronegative in character, possess a powerful precipitating action upon positive colloids, such as the sols of iron hydroxide now under consideration. It is only to be expected therefore that addition of salts to water in which iron is corroding will exert a triple effect, namely:

1. Accentuate the rate of solution of the iron by ionic activity —process 1, p. 133. This explains the rise in the curve to the maximum or "critical" point.
2. When the salt concentration is sufficiently great to exert

[1] Friend and Barnet, *loc. cit.*

a precipitating action upon the catalytic colloid, iron hydroxide, a retarding action will set in.

3. At high concentrations, also, the reduced solubility of the oxygen will tend to retard corrosion.

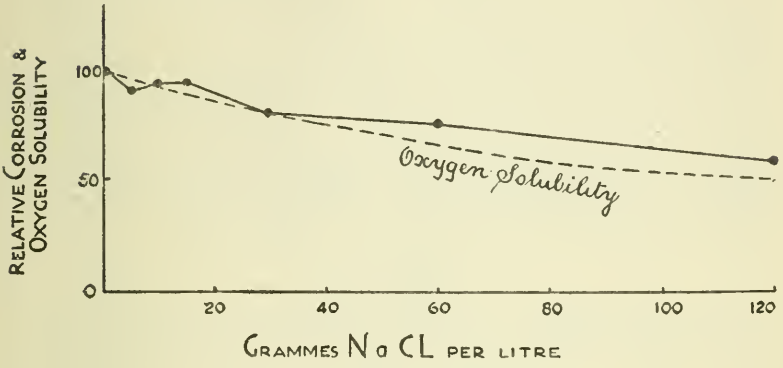


Fig. 6.

The actual extent of corrosion, therefore, at any special salt concentration is the result of the algebraic sum of the above factors.

Now if the above explanation is correct, it is evident that a definite similarity should be traceable between the influence of salts upon corrosion and their effect upon sols of iron hydroxide. Such is the case.

Numerous investigators have studied the precipitating effect of certain salts upon colloidal ferric hydroxide, and all agree that smaller quantities of bivalent anions (*e.g.* sulphates) are required than of univalent anions (*e.g.* chlorides) to precipitate their sols. The order of precipitation, as found by Linder and Picton,[1] is as follows :

	Relative Precipitating Power.
Chromates and dichromates	1000
Sulphates	670
Chlorides and nitrates (about equal) . . .	3

In other words, whilst very small quantities of chromates and bichromates will precipitate colloidal ferric hydroxide, large

[1] Linder and Picton, *Transactions of the Chemical Society*, 1905, vol. lxxxvii. p. 1906.

quantities of chlorides are essential, in view of their feeble coagulating powers. Sulphates lie intermediately.

It is therefore to be expected that small quantities of chromates and bichromates will serve to inhibit corrosion; large quantities of chlorides will be required to produce similar effects, and intermediate concentrations of sulphates.

That such is the case is abundantly evident from a consideration of the data in Table III., and shown in the form of curves in Fig. 7, in which the concentrations of the salts are expressed in terms of the acid radicle or gramme-anions per litre,[1] and the corrosion of iron in distilled water is taken throughout as 100, all other corrosions being expressed relatively thereto.

TABLE III.

Potassium Nitrate, 13·5° C.			Potassium Chloride, 15° C.			Potassium Sulphate, 15° C.		
Grammes KNO_3 per Litre.	Gramme-Anions per Litre.	Relative Corrosion.	Grammes KCl per Litre.	Gramme-Anions per Litre.	Relative Corrosion.	Grammes K_2SO_4 per Litre.	Gramme-Anions per Litre.	Relative Corrosion.
0	0	100	0	0	100	0	0	100
15	0·15	183	15	0·2	149	5	0·03	70
50	0·50	210	50	0·67	155	10	0·06	115
150	1·50	133	150	2·0	88	15	0·09	120
240	2·40	114	300	4·0	16	50	0·29	23
						100	0·58	14
Sodium Chloride, 16° C.			**Sodium Sulphate, 15° C.**			**Barium Chloride, 15° C.**		
Grammes NaCl per Litre.	Gramme-Anions per Litre.	Relative Corrosion.	Grammes Na_2SO_4 $10H_2O$ per Litre.	Gramme-Anions per Litre.	Relative Corrosion.	Grammes $BaCl_2$ $2H_2O$ per Litre.	Gramme-Anions per Litre.	Relative Corrosion.
0	0	100	0	0	100	0	0	100
1	0·02	104	5	0·02	112	5	0·04	111
5	0·09	130	15	0·05	163	15	0·12	121
50	0·85	124	50	0·16	161	50	0·41	111
120	2·04	89	100	0·32	59	100	0·82	62
200	3·40	42	200	0·63	35	250	2·05	30
360	6·12	8	300	0·95	23			

Very small quantities of potassium bichromate entirely inhibit corrosion.

It is now clear why the oxygen solubility curve in Fig. 5 differs from the corrosion curve, for the precipitating action of

[1] Recalculated from the data given by Friend and Barnet, *loc. cit.*

the potassium sulphate is superimposed upon the retarding effect of reduced oxygen solubility. In the case of sodium chloride, however, the precipitating action of this salt is relatively small, so that the corrosion curve is not so far removed from the oxygen-solubility curve in Fig. 6.

The nature of the metal or positive ion undoubtedly exerts an influence too, although less important than that of the acid

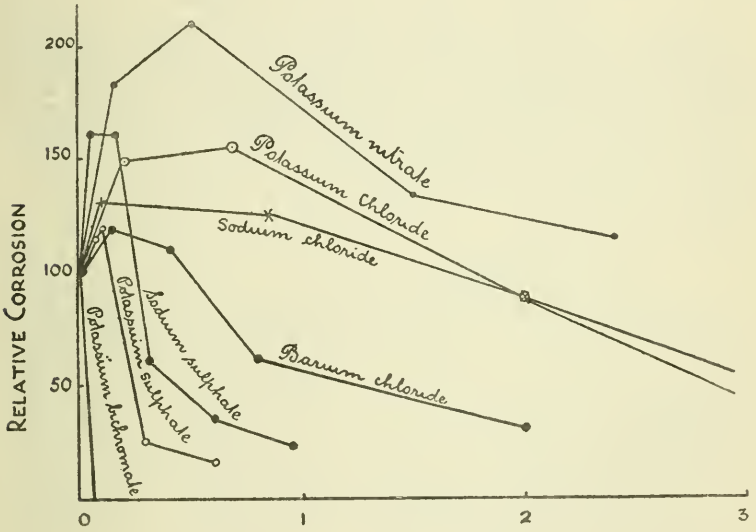


Fig. 7.

radicle or negative ion. For example, Hardy [1] found that the concentration of barium chloride required to precipitate ferric hydroxide sol lies intermediately between that of sodium chloride and potassium sulphate. The curves in Fig. 7 show in a very striking manner a similar parallelism.

The action of solutions of the alkali carbonates upon iron is one of peculiar interest. It has long been known that solutions of sodium carbonate retard the corrosion of iron. Indeed iron may be kept bright for indefinite periods in 1 per cent. solutions even when exposed to air. According to the acid theory

[1] Hardy, *Proceedings of the Royal Society*, 1900, vol. lxvi. pp. 95, 110.

this is due to the salt absorbing any atmospheric carbon dioxide, yielding the bicarbonate, $NaHCO_3$, so that there is no free carbon dioxide to act as catalyst. Whitney's theory explains the phenomenon on the ground of hydrolytic dissociation, the presence of the hydroxyl ions exerting a kind of back pressure and preventing the following reaction from occurring in the direction of left to right:

$$Fe + 2H^{\cdot} + 2OH' \leftarrow Fe^{\cdot\cdot} + H_2 + 2OH'.$$

Neither of these theories, however, will explain the fact noted by Cribb and Arnaud [1] in 1905 and by Heyn and Bauer [2] in 1908 that dilute solutions of sodium carbonate not only fail to retard corrosion, but actually accelerate it. The latter investigators obtained the following results at room temperature:

	Grammes Na_2CO_3 per Litre.
Critical concentration	1·0
Limiting concentration	below 10

Neither of the above theories can explain this observation, but the colloid theory disposes of the anomaly. The dilute solutions accelerate corrosion by their solvent action on the metal, just in the same manner as other salts. The inhibition of corrosion in solutions of 1 per cent. concentration and above is due to the powerful precipitating action of the alkali carbonate upon the colloid catalyst, the sol of iron hydroxide. The limiting concentration is so low that the effect of reduced oxygen solubility is negligibly small.

Sodium hydroxide behaves in an analogous manner when exposed to the atmosphere. The precipitated sol dissolves in the alkali, yielding, probably, an alkali ferrite which is ultimately thrown out as $Fe_2O_3Aq.$, but not on the surface of the metal. In this manner it is easy to account for the slow solubility of iron in caustic soda solutions, unaccompanied by rusting, which the author has observed even in relatively dilute solutions after the lapse of several years.

Influence of Temperature upon Corrosion.

Colloidal ferric hydroxide is so stable that the pure suspensoid in water may be boiled without precipitation. If small quantities

[1] Cribb and Arnaud, *Analyst*, 1905, vol. xxx. p. 225.
[2] Heyn and Bauer, *loc. cit.*, 1908, vol. xxvi p. 1.

of a salt are added, however, precipitation readily takes place. It is to be expected, therefore, that the rate of corrosion of iron will rise rapidly with the temperature in common with all exothermic reactions and, in the case of completely submerged specimens, where fairly pure water alone is the liquid phase, the point of maximum corrosion will be almost entirely dependent upon the ease with which oxygen can gain access to the metal. This latter is largely a function of the solubility of the gas. Experiments agree with this expectation, as shown in Part IV., the point of maximum corrosion occurring, under the conditions of the experiment, at about 80° C., the rate of corrosion being then more than seven times as great as that at 0° C.

In the presence of dissolved salts, however, the reactions are more complicated. Owing to the enhanced precipitating action of salts with rise of temperature, their critical concentrations fall, and relatively to water at the corresponding temperatures the corrosive action of the solutions also falls.

The steady fall of the critical concentrations is well illustrated by the following data :

Salt.	Temperature, °C.	Critical Concentration. Grammes/Litre.
Barium chloride ($BaCl_2.2H_2O$)	6	50
	12	50
	15	15
	18	5
	24	5
Potassium chloride (KCl)	3·5	50
	10	50
	15	15
	18	15
	23	5
Potassium nitrate (KNO_3)	5	50
	9·5	50
	13·5	15
	18	1
	23	1

An explanation is thus forthcoming for the very interesting fact that whilst a 3 per cent. solution of common salt is appreciably more corrosive at 5·6° C. than tap water at 19·6° C., there is little to choose between the two. This is shown by the following

data, obtained by suspending sets of three plates each in large tanks (40 litres) of Birmingham tap water and 3 per cent. sodium chloride solutions respectively, at different temperatures. The plates were made of mild steel and measured 4 inches square. They weighed approximately 22 grammes, and were exposed for three weeks.

TABLE IV.

All weighings are expressed in milligrammes.

No.	Liquid.	Temperature, °C.	Loss in Weight.	Duration of Test. Hours.	Mean[1] Loss per Hour.	Relative Corrosion.
1	water	5·6	317	504	0·3306	100
2			340			
3			332			
4	3 per cent. salt solution	5·6	515	504	0·5080	154
5			517			
6			488			
7	water	19·6	522	502	0·531	100
8			531			
9			541			
10	3 per cent. salt solution	19·6	558	502	0·555	105
11			600			
12			506			

These results are very striking; the more so inasmuch as they are incapable of explanation by the earlier theories.

Action of Alcohol.

The action of alcohol on iron is interesting in view of the use of steel tuns as containers. Up to the present experiments have only included mixtures of water and pure ethyl alcohol. If the oxygen solubility in the mixtures were the only factor, or even the most important one to be considered, the corrosion curve should follow the solubility curve. As shown in Fig. 8, however, this is not the case. The solubility curve (broken line) falls to a minimum and then rises rapidly. It is drawn to half scale in the

[1] Correcting for fluctuations in barometer as indicated in Part IV.

diagram for convenience of representation. The corrosion curve (continuous line), on the other hand, rapidly falls, until with absolute alcohol corrosion ceases.

The colloid theory offers a satisfactory explanation. Alcohol possesses considerable dehydrating power, and is able to effect the precipitation of hydrated sols by withdrawing the water.

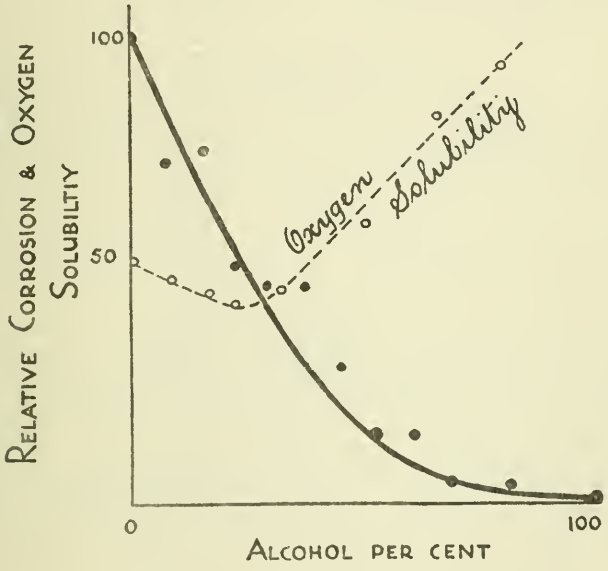


Fig. 8.

Hence the alcohol tends to precipitate the catalyst—colloidal ferric hydroxide—and to retard corrosion.

Action of Poisons.

It is well known that catalysed reactions may be hindered or even stopped by the addition of small quantities of certain substances, which are termed "poisons." The poison appears to attack, or be superficially adsorbed by, the catalyst, which is thereby rendered inert. Most of these poisons are actually poisonous to the animal system, whence their name.

Now colloidal ferric hydroxide readily adsorbs arsenious oxide, and has been recommended as an antidote in cases of arsenical

poisoning for that reason. It is most suggestive, therefore, to find that arsenious oxide is a powerful inhibitor of corrosion.[1] This is readily understood if the colloid theory is accepted, for the arsenic will tend to paralyse the colloidal iron hydroxide and to inhibit the corrosion. Sodium arsenite will behave similarly, and the custom of adding this to boiler feed-waters to reduce corrosion [2] thus receives theoretical support.

Action of Radium Rays.

Were the corrosion of iron a purely ionic effect, exposure to radium rays should lead to an acceleration of corrosion, for it is well known that oxidation processes are usually very sensitive in this respect. On the other hand, radium rays tend to precipitate iron hydroxide sol. If, therefore, the colloid theory is correct, exposure to radium should retard corrosion.

Experiments were arranged to test this. A small metal capsule containing 0·1 milligramme of radium chloride was suspended above a shallow earthenware dish containing a disc of pure electrolytic iron foil, as shown in Fig. 9. The experiment was repeated several times, the height, h, being varied, and blanks were simultaneously run. The results clearly indicated a decided retardation of corrosion, despite the extremely feeble source of rays. Thus :

Height, h (centimetres) . .	∞	13	4
Relative corrosion . . .	100	87	85

Influence of Protective Colloids.

The colloid theory of corrosion is of particular technical interest in that it opens up a new method of attacking the important problem of the preservation of iron. It is now evident that it is not absolutely essential to exclude water or air from contact with the metal. Corrosion may be entirely prevented by the presence of some force, whether chemical or physical, which will precipitate or otherwise destroy the colloid catalyst. Electrical energy may be used, the iron being rendered cathodic by passage

[1] See Lindet, *Comptes rendus*, 1904, vol. cxxxix. p. 859, confirmed by later investigators.

[2] Huntley, *Journal of the Society of Chemical Industry*, 1909, vol. xxviii. p. 339.

of a current. Contact with zinc or other highly electropositive metal produces a like effect.

It is a common statement that "busy iron does not rust." Various explanations have been offered, but probably the real cause lies in the now well-recognised tendency for vibratory motion to effect the precipitation of colloids. The catalytic hydroxide sol is thus coagulated practically as rapidly as it is produced, so that corrosion is proportionately retarded.

The influence of protective colloids has been made the subject of considerable study, and the results are of importance. Protective colloids are usually organic in character,

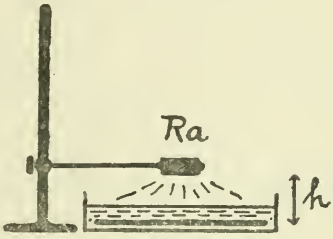


Fig. 9.

glue and starch being typical examples. The author has shown that dilute solutions of these tend to retard the corrosion of iron immersed in them.[1] The following results were obtained by exposing plates of Kahlbaum's electrolytic iron foil to the action of dilute solutions (0·2 per cent.) of the colloids in water for sixteen days:

	Relative Corrosion.
Water	100
Gum arabic (acacia)	63
Potato starch	50
Dextrin	50
Gelatin	50
Egg albumen	28
Agar	10

This retarding action is not confined to the corrosion of iron. It has been found by Mr. R. H. Vallance, B.Sc., and the author to obtain with other common metals such as lead, zinc, and aluminium. The results are of considerable interest, since in most culinary operations colloidal substances are dealt with

[1] Friend, *Transactions of the Chemical Society*, 1921, vol. cxix. p. 932.

which pass into the waters and thus retard the corrosion of the utensils.

The retardation increases with the concentration of the colloid, and corrosion becomes negligibly small when the disperse phase is so concentrated as to yield a jelly or "gel." The explanation appears to lie in *adsorption*;[1] that is, an excessively thin layer of the colloid is attracted to the metallic surface and more or less completely covers it, thus proportionately preserving it from attack both by hindering the formation of the colloid hydroxide catalyst, and by retarding its activity when formed. The more concentrated the colloid solution, the more complete the coating, and hence the more efficient the preservation.

Herein lies the explanation for the efficiency of paints made with linseed oil. The oil "sets" to a gel, which is strongly adsorbed by the metallic surface, and which therefore affords a very thorough protection to the same (see Part II.).

An interesting case arises when dissolved salts are present in the waters containing the protective colloids. At first the action of the salts is but small, but as the concentration rises it gradually increases, until, at high concentrations, the protective colloid is "salted out," and the results are the same as if no colloid were present. This is well illustrated by the curves shown in Fig. 10, which represent the relative corrosions of plates of pure iron foil immersed for twelve days in solutions of potassium sulphate of varying concentration at 10° C. The continuous line gives the results in the absence of a protective colloid, whilst the broken line gives those obtained in the presence of 1 per cent. gum acacia. At a salt concentration of 60 grammes per litre the colloid has been practically salted out, and the two curves meet. The numerical data are as follow:

Grammes K_2SO_4 per litre	0	1	5	10	15	25	60
Relative corrosion—							
(i) Aqueous solution .	100	100	119	109	151	158	85
(ii) Acacia solution .	47	57	81	94	76	86	81

It will be observed that the fall in corrosion in the case of the non-colloid solution at a concentration of 10 grammes of potas-

[1] In support of this may be mentioned the fact that the data are found to obey the adsorption law (Friend and Vallance, *Transactions of the Chemical Society*, 1922, vol. cxxi. p. 466).

sium sulphate is reflected in the acacia solution at 15 grammes concentration.

In the majority of cases of corrosion in practice such high concentrations of salts as are necessary to salt out the colloid do not usually occur, and colloidal matter may with advantage be added to waters to inhibit corrosion provided the colloids are of such a nature as not to chemically decompose in service yielding corrosive products. Thus fatty oils should not be used in

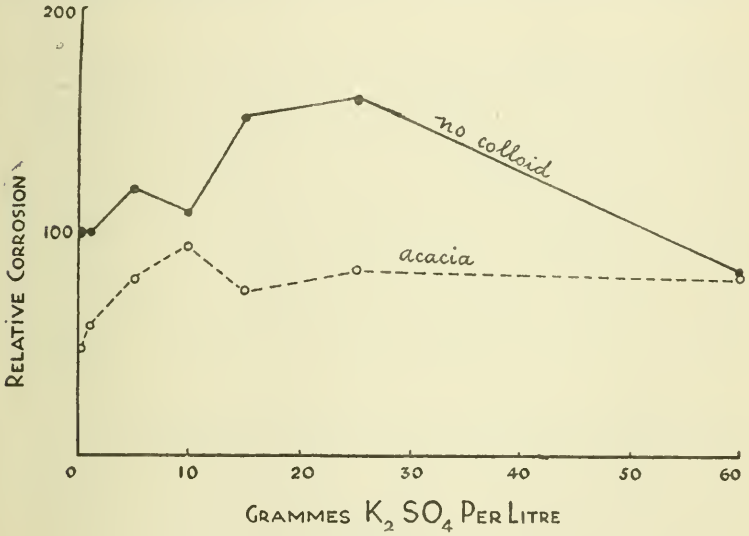


FIG. 10.

boiler practice, as these yield corrosive acids under working conditions. But the practice of boiling bones in an iron boiler before the latter is actually connected up for service has much to recommend it, since the gluey colloids which dissolve out into the water are adsorbed by the metal and tend to protect it from corrosion.

CONCLUSION.

The colloid theory of corrosion offers satisfactory explanations for many phenomena which cannot be explained by any of the older theories. It also suggests new lines of attacking the problem of the protection of iron and steel from oxidation.

APPENDIX

PRELIMINARY REPORT ON THE RELATIVE CORRODIBILITIES OF VARIOUS COMMERCIAL FORMS OF IRON AND STEEL.

The question as to which is the more resistant to corrosion, iron or steel, is one which has continually exercised the minds of both manufacturer and purchaser during the last hundred years. The earliest researches carried out on the subject on a large scale were those of Mallet in 1840. Since that date many other investigations have been published, some leading to one result and others to an exactly opposite one. The subject, however, is always new, for each fresh method of manufacture, indeed each modification of old methods, is liable to produce a metal differing in its powers of corrosion-resistance from those hitherto examined.

The problem of determining the relative corrodibilities of two or more classes of metal is very much more difficult than would at first sight appear. This will be evident from the following:

1. *What Standard of Corrosion is to be Adopted?*—Almost all the early researches were confined to a consideration of the losses in weight undergone by the metals when the rust produced during exposure to various corroding media had been removed. This is a favourite method at the present time in laboratory tests, and in the absence of pitting yields very valuable and trustworthy results. This method presupposes a knowledge of the weight of the metal prior to exposure to corrosion, and in most cases in practice this is entirely out of the question. Hence this method is largely confined to laboratory or special "field" tests.

On the other hand, some metals are particularly liable to suffer from pitting, and certain media—notably faintly alkaline waters containing dissolved salts—will induce pitting in almost any forms of iron. In such cases the loss in weight might be negligibly

small, but if the metal were perforated it might, as in the case of pipes and boilers, lead to disastrous consequences. Hence mere loss in weight is not in itself the only factor to be considered. The extent and depth of pitting should also be ascertained.

2. *The Selection of truly Representative Samples of Metal.*—This is a task of considerable difficulty, and no doubt many of the incongruities of earlier researches have arisen from the fact that investigators have not worked with a sufficient number of typically representative samples of metal. In the present research this difficulty has been largely overcome, as indicated on p. 152.

3. *Method of Conducting the Corrosion Tests.*—This should always be specified, for it is now well established that no one metal will resist equally satisfactorily all kinds of corroding media. This is well illustrated by stainless steel (see HS, Table I.), which is highly resistant to tap water, but is very susceptible to attack by sulphuric acid. It is thus eminently desirable that laboratory tests should be made to resemble as closely as possible the conditions to which the metals will be exposed in practice. No quantitative data correlating laboratory tests and practical experience have been published, so far as the author is aware, but it is hoped that the present research will enable laboratory and field tests to be correlated, and indicate the best methods of standardising laboratory practice.

White Iron Rust.

As a general rule iron rust, when produced in the presence of excess air, is brown. If in thick layers, those portions nearest the unattacked metal may be bluish black. The author has succeeded in preparing perfectly white rust.

Faintly alkaline solutions containing dissolved salts in small quantity, such as sodium chloride, readily induce pitting in even the purest forms of iron and steel. Normally patches or filaments of rust, blue in colour, originate at some spot on the surface of the submerged metal, and consist mainly of hydrated ferrous oxide, darkened with small amounts of higher oxide. As corrosion proceeds and increasing quantities of air diffuse down to the rust, the uppermost portions are oxidised to the characteristically

brown hydrated ferric oxide. If, however, the amount of air diffusing to the metal is restricted, as, for example, by suspending a long strip of steel (say 2 feet in length) vertically in a glass tube filled with solution, the oxygen of the air will not be able to reach the lower part of the metal as rapidly as the latter can absorb it, and small patches of almost pure hydrated ferrous oxide, perfectly white in colour, are produced.

Scope of the Research.

The aims of the present research are three in number, namely:

1. To determine by means of "field tests" the relative corrodibilities of various commercial forms of iron and steel under varying conditions of exposure.
2. To determine in a similar manner the relative corrodibilities of the more important non-ferrous metals and some of their alloys.
3. To carry out simultaneously several series of laboratory tests to ascertain whether or not they yield results comparable with the field tests, and hence to obtain an indication as to their value in practice.

Supplies of metal have therefore been acquired amounting in all to forty different kinds of iron and steel, including some of the more common types of special steel, and seventeen non-ferrous metals and alloys. Some of these have been obtained by purchase, the cost having been defrayed by a grant from the Carnegie Scholarship Fund of this Institute. The author desires to take this opportunity of thanking the committee for their generous support, which has made possible the carrying out of this research. The majority of the ferrous metals, and the whole of the non-ferrous metals and alloys, have been generously given to the author by various firms, whose kindness is here gratefully acknowledged. All the metals are in the form of round bars, $1\frac{1}{4}$ inches in diameter, and have been cut into 2-foot lengths.

These bars are, in the case of the field tests, being weighed and placed in large wooden frames specially constructed for the

purpose, and exposed to corrosion under varying conditions. Arrangements for these are not yet quite complete. The exposures will be continued for several years, at the end of which time the bars will be removed, cleaned, and weighed, their loss through corrosion being thereby determined. Depth of pitting, change in composition—more particularly in the case of alloys—and any other points of interest will be duly recorded. The data thus obtained should enable useful comparisons to be drawn between various ferrous and non-ferrous metals from the point of view of their corrodibilities.

Several series of laboratory tests are being carried out, namely with longitudinal and with transverse sections of the metals, with strained and unstrained pieces, &c. It is hoped that, as a result of comparing the data so obtained with those from the field tests, it may be possible to standardise the different laboratory methods now in use for determining the rates of corrosion in various media, and thus to render the data obtained by different investigators more truly comparable and useful.

Results of Laboratory Tests.

Laboratory tests have, up to the present, only been carried out with transverse slices from bars of thirty-five different kinds of iron, steel, and nickel, namely:

1 commercially pure iron.
12 wrought irons.
9 carbon steels.
9 special steels.
3 cast irons.
1 metallic nickel.

The slices measured 1·12 inches in diameter, were approximately 0·2 inch thick, and weighed about 20 grammes. Each disc was carefully measured and its superficial area calculated.[1] After weighing it was laid on a piece of paraffin wax and exposed to corrosion.

[1] It has been assumed in this investigation that the rate of corrosion is directly proportional to the area exposed. This is correct, within the error of experiment, when the differences in area are small.

Four different tests were carried out with as many different discs of each kind of metal, namely :

1. Continuous immersion in Birmingham tap and rain water in a large tank exposed to the open air. Duration, four months.
2. Alternate wet and dry in a large tank in the laboratory which alternately filled and emptied itself about every two hours. Duration, four months.
3. Continuous immersion in artificial sea-water. Duration, four months.
4. Continuous immersion in 20 litres of 0·5 per cent. sulphuric acid. Duration, twenty-two hours.

The results are given in Table I.

In considering these results the author desires to lay special emphasis upon the fact that the specimens tested were in the form of transverse discs. This is a point of great importance in so far as the wrought irons are concerned, as the grain in these metals is very pronounced. In the case of cast iron and steel the matter is much less important. Experiments are being conducted with cylindrical bars of the same metals with a view to determining their relative corrodibilities under longitudinal exposures, which are normally those obtaining in practice.

Bearing this limitation in mind, the following observations appear worthy of consideration :

1. The different varieties of wrought and cast irons, and of carbon steels, corrode in neutral media with remarkable uniformity. For the sake of clearness the mean values are given below :

	Tap Water.	Alternate Wet and Dry.	Sea-Water.	Mean Relative Corrosion.
Wrought irons . . .	104·5	193·8	85·7	100·0
Carbon steels . . .	102·7	202·7	87·9	102·4
Cast irons . . .	110·3	201·1	86·4	103·6

The " skins " had necessarily been removed from the cast irons, so that they were more susceptible to attack than usual. Nevertheless they are seen to have resisted corrosion quite as

Table I.

All weighings are expressed in grammes.

Identification Mark.	Metal.	Continuous Tap Water.			Alternate Wet and Dry.			Sea-Water.			0·5 per cent. H_2SO_4.		
		Loss.	Loss per 1000 Sq. Inches.	Mean.	Loss.	Loss per 1000 Sq. Inches.	Mean.	Loss.	Loss per 1000 Sq. Inches.	Mean.	Loss.	Loss per 1000 Sq. Inches.	Mean.
A1	Commercially pure iron	0·154	96·0		...	...		0·134	79·6		0·130	76·1	
EB	Wrought irons	0·177	105·4		0·319	192·9		0·132	84·3		1·118	702·7	
EBB		0·167	102·2		0·296	195·5		0·124	80·0		1·064	744·6	
EBC		0·181	104·4		0·292	176·5		0·137	88·4		1·089	672·6	
EC		0·182	108·3		0·303	184·3		0·136	81·6		0·952	633·0	
HA		0·182	106·6	104·5	0·303	180·0	193·8	0·156	92·3	85·7	0·825	456·1	461·3
HB		0·166	104·8		0·305	196·9		0·135	85·7		0·607	378·9	
HBB		0·175	100·4		0·338	196·7		0·141	84·9		0·693	437·5	
HBBB		0·174	107·3		0·323	200·0		0·146	88·3		0·776	445·2	
HC		0·175	98·2		0·348	200·5		0·144	85·6		0·517	324·1	
L		0·158	105·5		0·309	203·2		0·124	84·1		0·481	303·9	
RBB		0·149	102·3		0·292	192·9		0·125	81·9		0·349	238·9	
RBB		0·198	108·3		0·360	206·2		0·164	90·9		0·381	197·9	
DU	Carbon steels	0·172	105·3		0·334	219·2		0·136	88·0		0·381	232·3	
DV		0·171	101·5		0·307	203·7		0·131	86·7		0·199	127·2	
H1		0·155	100·6		0·292	189·8		0·139	87·6		0·217	131·2	
H2		0·188	101·9		0·357	202·0		0·155	88·9		0·292	163·9	
H3		0·156	98·9	102·7	0·322	207·9	202·7	0·145	86·4	87·9	0·364	233·5	231·3
RM		0·184	109·7		0·339	192·2		0·119	91·4		0·400	217·3	
RS		0·143	94·3		0·296	191·1		0·132	82·0		0·735	497·3	
WH		0·184	105·4		0·358	211·4		0·136	96·1		0·592	352·4	
WM		0·183	106·9		0·367	207·2		0·146	84·3		0·194	126·9	

TABLE I.—*Continued.*

Identification Mark.	Metal.	Continuous Tap Water.			Alternate Wet and Dry.			Sea-Water.			0·5 per cent. H_2SO_4.		
		Loss.	Loss per 1000 Sq. Inches.	Mean.	Loss.	Loss per 1000 Sq. Inches.	Mean.	Loss.	Loss per 1000 Sq. Inches.	Mean.	Loss.	Loss per 1000 Sq. Inches.	Mean.
	Special Steels.												
HCU	Cu 0·15	0·165	101·3		0·378	212·2		0·119	78·8		0·111	73·3	
HS	"Stainless"	0·011	6·3		...	...		0·073	41·3		0·297	183·0	
K1	Ni 4, Cr 1.	0·164	99·6		0·258	159·2		0·160	93·7		0·214	126·6	
S2	...	0·179	94·2		0·257	142·8		0·163	85·9		0·174	87·8	
S8	Ni 2·5	0·170	94·3		0·307	169·3		0·157	84·3		0·124	68·8	
S10	Ni 2·5	0·190	101·1		0·362	201·7		0·186	102·6		0·318	168·9	
S16	Ni 4, Cr 1.	0·167	104·7		0·253	158·6		0·128	78·0		0·416	268·6	
S17	Ni 5, Cr 0·25	0·160	93·3		0·275	157·1		0·140	80·0		0·072	43·3	
S19	Cr 11·5	0·028	14·9		0·042	22·9		0·062	34·9		0·499	270·0	
CA	Cast irons	0·203	115·3		0·360	206·2		0·137	86·1		2·252	1354·6	
CC		0·199	110·2	110·3	0·380	209·6	201·1	0·166	94·2	86·4	2·435	1343·1	1325·6
W1		0·206	105·4		0·340	187·5		0·143	78·9		2·506	1279·2	
Ni	Nickel	0·009	4·9		0·011	6·4		0·041	22·5		0·006	3·0	

well as the steels in all but the tap-water tests. The wrought irons and carbon steels are remarkably similar in their powers of resistance, although in the alternate wet and dry tests the wrought irons show somewhat to advantage.

2. In the acid tests (Table I.) the wrought irons are less resistant than the steels, whilst the cast irons are even more seriously attacked.

3. The commercially pure iron is highly resistant to acid attack, and is quite as resistant to neutral corrosion as the wrought irons. The cupriferous steel (HCU) is equally resistant to acid attack and compares favourably with the wrought irons in neutral media, save that in alternate wet and dry it is slightly more corroded. The nickel and nickel-chrome steels show favourably in the alternate wet and dry, and in the acid tests. In tap water and sea-water they behave in much the same way as the carbon steels, thus confirming the conclusion arrived at in earlier work that unless the percentage of nickel exceeds 3 or 4, its effect is small. Steel S19 is highly resistant to neutral media.

4. The stainless steel is remarkably resistant to tap water, less so to sea-water, and fairly soluble in acid, in this latter respect comparing with the carbon steels. Metallic nickel itself appears very resistant to all the types of corrosion tried, the sea-water having the most effect.

The above results harmonise very well with those of earlier researches. Critical discussion of the same is withheld until further data have been accumulated.

NAME INDEX

Adeney, 118
Adie, 135, 136
Aitchison, 112
Andrew, 13
Andrews, 47–49, 71–74, 103, 104
Armstrong, 116
Arnaud, 116, 140
Arndt, 58, 59, 61
Aston, 27, 31, 53, 54, 66, 67

Barnet, 135, 136, 138
Barus, 103
Bauer, 6, 21, 23, 24, 27, 30–35, 50–53, 61–66, 75–78, 108, 113, 127, 135, 140
Becker, 118
Behr, 104
Bent, 115
Bentley, 75, 106, 116
Bergius, 6
Berthier, 26
Berzelius, 2
Bolis, 19
Burgess, 27, 31, 53, 54, 66, 67, 103
Byers, 83

Calvert, 5, 125
Carson, 81
Carulla, 11, 19
Catch, 10, 12, 28
Cederholm, 115
Chappell, 112
Cribb, 116, 140
Cumming, 13, 14

Daniell, 5, 8, 12, 28
Davis, 10
Davy, 79
Dennett, 130
Desch, 14
Diegel, 34
Dill, 103, 104
Draper, 4
Dunstan, 125

Freund, 6
Fryer, 19

Gaines, 81, 82, 85
Gerhard, 84
Gruner, 45, 46, 65, 66
Grzeschik, 6

Haber, 14
Hadfield, 112
Hambuechen, 103, 105
Harbord, 28
Hardy, 139
Hargest, 10, 12, 28
Hatfield, 129, 130
Henry, 8
Heyn, 27, 31–35, 50–53, 61–66, 75–78, 108, 113, 127, 135, 140
Holde, 20
Huntley, 144

Jackson, 19
Johnson, F., 10
Johnson, W. H., 12
Jouve, 12
Jüngst, 81

Kahlbaum, 107
Kempson, 19
Knietsch, 10, 13
Kohn, 6
Kowalke, 36
Krassa, 6
Kröhnke, 9, 58

Larsson, 10
Ledebur, 13
Le Naour, 5
Lidy, 4
Liebreich, 95
Linder, 137
Lindet, 144
Lloyd, 79
Lowry, 107
Lunge, 9

MacArthur, 135
McWane, 81
Mallett, 2, 5, 6, 8, 9, 22, 26, 28, 35, 38–44, 70, 71, 76, 78, 113, 149
Marshall, 36, 37, 54, 55, 67, 68, 106
Menzel, 18
Moody, 17, 127
Moorfield, 106
Mulder, 79

Parker, 107
Pepys, 6
Percy, 2, 5, 8
Pick, 14
Picton, 137
Piwowarsky, 30, 33
Poggendorf, 14
Porlier, 5
Prost, 12

Rennie, 3
Reynolds, 12
Richards, 104
Richter, 8

Scheurer-Kestner, 17
Schleicher, 69
Schultz, 69
Spitzer, 95
Spring, 134
Stead, 10, 28, 36
Stewart, 79
Sturm, 107

Thénard, 17
Thwaite, 44, 45
Tilden, 9
Turner, 6, 9, 10, 14, 28, 35, 36

Vallance, 96, 145, 146
Van Beck, 79
Venator, 14, 15

Walker, 103, 104, 115, 135
West, 75, 116
Wetzel, 6, 21–24
Whitney, 126, 127, 140
Wilkinson, 3
Wölbling, 60, 61
Wood, 12

SUBJECT INDEX.

Acacia gum retards corrosion, 145–147
Acetic acid, influence of, 5
Acid theory of corrosion, 125–6
Acids, action on cast iron, 5, 6, 8–14, 28, 29, 65–70, 153–156
  brittleness caused by, 12, 13
Adsorption, 146
Agar retards corrosion, 145
Albumin retards corrosion, 145
Alcohol and corrosion, 142, 143
Alkalies, action of, on cast iron, 14
Alloying elements, influence of, 25–37
American foundry rules for retarding corrosion, 85
Ammonia stills, 19
Ammonium sulphate, influence of, 18
Arsenic, influence of, on iron, 26, 27

Barium chloride, influence of, 138, 139
Brass, contact influence of, 77
Brine, action of, on cast iron, 18
Bursting of cast iron, 13

Calcium chloride, influence of, 19
Carbon content and corrosion, 27, 112
Carbon tetrachloride, influence of, 19
Carbonic acid, influence of, 69
Carbonic acid theory, 126
Cast iron—
  action of acids on, 5, 6, 8–14, 28, 29, 65–70, 153–156
  ——— alkalies on, 14
  ——— alloying elements, 25–37
  ——— ammonium sulphate on, 18
  ——— arsenic in, 26
  ——— calcium chloride on, 19
  ——— carbon tetrachloride on, 19
  ——— carbonic acid on, 69
  ——— caustic soda on, 15–17
  ——— chromic acid on, 14
  ——— coffee vapour on, 6
  ——— cobalt in, 29
  ——— dilute acids on, 5, 6, 8–14, 28, 29, 65–70
  ——— electric current on, 6–8
Cast iron—*continued*
  action of hydrochloric acid on, 5, 11, 44
  ——— hydrogen peroxide on, 17
  ——— hydrogen sulphide on, 18
  ——— manganese in, 31, 32, 35
  ——— natural brine on, 18
  ——— nickel in, 33
  ——— oils on, 20
  ——— oxygen absorbed by, 57–61
  ——— phosphorus in, 34
  ——— proof spirit on, 6
  ——— pyroligneous acid on, 6
  ——— silicon in, 9, 25, 35–37
  ——— skin on, 40, 41, 45
  ——— sulphur in, 25, 28
  ——— sulphuric acid on, 5, 6, 8–11, 28, 29, 65–68
  ——— sulphuric acid, fuming, 13
  ——— tannic acid, 12
  ——— wine on, 6
  brine on, 18
  brittleness, 13
  bursting of, 13
  carbon in, 27–29
  chilled, 9, 28, 29, 40–44, 85
  corrosion of, 11
  galvanised, 45
  graphitisation of, 2–8
  grey, behaviour of, 9, 28, 29, 71, 153–156
  pitting of, 54
  relative corrosion, 153–156
  white, corrosion of, 9, 28, 29, 40–44, 70, 71
Caustic soda, influence of, 15–17
Centralia conduit, 83
Chilled cast iron, 9, 28, 29, 40–44, 85
Chromic acid, influence of, 14
Cobalt in iron, influence of, 29
Colloid theory, see Part V.
Colloids retard corrosion, 145
Copper contact, influence of, 8
——— in steel, 153–156
Corrosion—
  acid theory of, 125–6
  carbonic acid theory of, 126
  colloid theory of, see Part V.

Corrosion—*continued*
determination of, gravimetric, 38
——— volumetric, 57
electrolytic theory, 126
factor, 38
humidity and, 118
index, 38
influence of dissolved salts on, 135–147
——— illumination on, 116
——— poisons on, 143
——— shape on, 22
——— strain on, see Part III.
in acid media, 65–69
in clay, 121
in moving media, 61–65
in neutral media, 37–61
in sand, 21
in service, 79–85
light, influence of, on, 116
liquid water essential to, 125
meaning of term, 1
pitting, 54, 84
potential difference and, 70–79
radium and, 144, 145
rate of, 42, 44, 51, 52
standard of, 150
temperature accelerates, 23–25. See also Part IV.
Critical concentration, 135
influence of temperature on, 144
Cupriferous steel, 153–156

Dextrin retards corrosion, 145
Direct action, 25

Egg albumen retards corrosion, 145
Electric currents, influence of, on cast iron, 6, 14
Electrolytic theory, 126
Energy absorbed in rupture, 103
Erosion, 2

Ferrite, behaviour of, with acids, 9
and alkalies, 9, 14

Galvanic action, 28, 40, 70–79
Galvanised iron, 45, 79
Gelatin retards corrosion, 145
Graphitic carbon, 27
Graphitisation, 2–8
Gum arabic retards corrosion, 145–147
Gun-metal, 79

Heat treatment of oil, influence of, 96
Historical instances of—
corrosion, 2–8
Armada, guns used in, 2
Brest Harbour, cannon balls from, 4
Dublin graving slip, 4
Edgar, The, guns from, 42
Florida, The, guns from, 2
John Bull, The, keel of, 3
Karlskrona, cannon balls from, 2
La Hogue, cannon balls from, 3
Mary Rose, The, guns from, 3
Humidity and corrosion, 118
Hydrochloric acid, influence of, on cast iron, 11, 12, 44
——— on steel, 12
Hydrogen peroxide, influence of, 17, 18
Hydrogen sulphide, influence of, 18

Illumination and corrosion, 116
Index of corrosion, 38
Indirect action, 25
Iron, protection of, with paint, see Part II.
—— wrought, see Wrought Iron.

Light accelerates corrosion, 116
Limiting concentration of salts, 135

Manganese, influence of, in cast iron, 31, 32, 35
Mill scale and corrosion, 98
Motion, influence of, on corrosion, 61–65, 127–133

Natural brine, influence of, on cast iron, 18
Nickel, influence of, 155
on cast iron, 33
on steels, 153–156

Oils, action of, on cast iron, 20
heat treatment of, 96
permeability to moisture of, 97
polymerisation of, 96, 97
relative proportion in paint, 89
Oxygen absorbed by cast iron, 57–61
dissolved, on corrosion, 135–139
pressure and corrosion, 115

Paint—
optimum composition of, 91
relative proportion of oil, 89
standard, 97
thick and thin coats, 92
Phosphoric acid, influence of, 6
Phosphorus in cast iron, influence of, 34, 35
Pigment, function of, in paint, 90
proportion of, in paint, 89
Pitting factor, 54
of cast iron, 54–84
Poisons, influence of, on corrosion, 143
Potassium chloride, influence of, 136, 138, 139, 141
——— nitrate, 138, 139, 141
——— sulphate, 138, 139, 146, 147
Potential difference and corrosion, 70–79
and strain, 103–106
Protective colloids and corrosion, 144–147
Pyroligneous acid, influence of, 6

Radium rays retard corrosion, 144, 145
Rate of corrosion, 42, 44, 51, 52
Relative corrosiveness of salt and fresh waters, 142
Relative corrosion of—
cast iron, wrought iron, and steel, 37–69, 153–156
grey and white iron, 9, 28, 29
sand cast and chilled iron, 28, 29
Rochester, U.S.A., relative behaviour of iron and steel conduit pipes, 82
Rust, white, 150

Scale, removal of, before painting, 98
Shape, influence of, on corrosion, 22, 41
Silicon, influence of, on cast iron, 9, 25, 35–37
Skin, influence of, on cast iron, 40, 41, 45
Sodium arsenite inhibits corrosion, 144
Sodium chloride, influence of, on, 137–139
Sodium sulphate, influence of, 138, 139
Spiegel, corrosion of, 46, 47
Stainless steel, 153–156
Starch retards corrosion, 145
Steel, brittleness induced by acids, 12
caustic soda, influence of, on, 15, 16
Steel, density, influence of, on, 107
hydrochloric acid, influence on, 12
contact, behaviour of, with cast iron, 75–79
influence of motion on, 61–65
relative corrosion of, 37–69, 153–156
solubility of, in acids, 108
strain, influence of, on, see Part III.
sulphuric acid, influence of, on, 11, 65–68, 109
Sulphuric acid, action on iron in motion, 130–133
concentrated, influence of, on cast iron, 10
dilute, influence of, on cast iron, &c., 5, 8, 11, 28, 29, 30, 33, 35–37, 65–68, 109
fuming, influence of, on, 13
Surrosion, 2

Tannic acid, influence of, 12
Temperature and corrosion, 23. Also Part IV. and 140–142
and critical concentration, 141
Thickness of cast iron and corrosion, 22, 41
of paint, influence of, on, 92
Time and corrosion, 42, 44, 51, 52
Tin, influence of, 79

White rust, 150
Whitney's theory, 126
Wrought iron—
action of acids on, 65–69
brittleness in, induced by acids, 12, 13
caustic soda, influence of, on, 15, 16
corrosion of, in moving media, 61–65
galvanic action, influence of, 70–79
relative corrosion of, 57–70, 153–156

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